Journal of Catalysis **187,** 191–201 (1999)
Article ID jcat.1999.2582, available online at http://www.idealibrary.com on IDEAL®

# Role of Amine Modifiers in the Epoxidation of Allylic Alcohols with a $TiO_2$–$SiO_2$ Aerogel

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Received April 6, 1999; revised June 2, 1999; accepted June 3, 1999

**A detailed study of the epoxidation of 3-methyl-2-cyclohexen-1-ol with *tert*-butylhydroperoxide revealed that the poor performance of a 20 wt% $TiO_2$–80 wt% $SiO_2$ aerogel was due to nonoxidative consumption of the allylic alcohol. Epoxide selectivities could be improved remarkably and acid-catalyzed side reactions suppressed by addition of small amounts of aliphatic, cycloaliphatic, or aromatic amines. The best modifier was *N*,*N*-dimethylbutylamine. Amine (1 mol%) enhanced the epoxide selectivities, related to the reactant or peroxide, from 3 to 99% and 35 to 100%, respectively. Kinetic investigations uncovered how the chemical structure and the amount of various amines influence the complex network of redox- and acid-catalyzed reactions during allylic alcohol epoxidations. The stability of amines was studied under oxidizing reaction conditions. The method of amine addition was applied also to the epoxidation of other linear and cyclic allylic alcohols and 2-hexene. The scope of this method seems to be limited to epoxidation of allylic alcohols. A model for the interaction of allylic alcohol, amine, and peroxide with the Ti active site is proposed, which can interpret the enhanced selectivity and suppressed activity in the presence of amines or other bases.** © 1999 Academic Press

## 1. INTRODUCTION

It is now established that nanoscale engineering of sol–gel $TiO_2$–$SiO_2$ mixed oxides provides excellent microporous (1, 2) or mesoporous (3, 4) epoxidation catalysts. A comparison of the catalytic performances of these amorphous oxides with molecular sieve materials has been reported in Ref. (5). Highly dispersed titania in the silica matrix, mesoporous structure, and high surface area are the key characteristics of the 20 wt% $TiO_2$–80 wt% $SiO_2$ aerogel obtained by this method (3). This catalyst showed outstanding performance in the epoxidation of cyclic olefins with alkylhydroperoxides (6). The application range of the aerogel could be extended to $\alpha$-isophorone possessing an electron deficient C=C double bond and to some allylic alcohols (7, 8). Generally, epoxide selectivities are often limited by various consecutive and parallel side reactions, such as the solvolysis of the epoxide (9), oxidation of a hydroxyl functional group (10), or various isomerization reactions (11). It was shown for TS-1, Ti-$\beta$, and the $TiO_2$–$SiO_2$ aerogel that the acid-catalyzed side reactions could be suppressed when the residual Brønsted acidity of the catalyst was neutralized by alkali metal exchange (9, 11, 12), albeit often with concomitant loss of activity. The simple addition of solid inorganic bases to the reaction mixture represents a recent development in this direction. Even weak bases, such as $NaHCO_3$, which are poorly soluble in the apolar reaction medium, had a remarkable positive effect on selectivity in the epoxidation of $\beta$-isophorone (11) and some allylic alcohols (8).

Amines can also be used as basic additives. Hydration of the epoxide to glycol during oxidation of cyclohexene with a $TiO_2$–$SiO_2$ mixed oxide and $H_2O_2$ was suppressed with small amounts of urea, $Bu_4NOH$, or isoquinoline (4). The enhanced selectivity and reduced activity observed in the presence of N-bases was explained by the effect on Lewis acidity of the catalyst. Note that amines are widely used in heterogeneous catalytic oxidation and hydrogenation reactions as selective modifiers. An example from the recent literature is the selective oxidation of L-sorbose to 2-keto-L-gulonic acid over $Pt/Al_2O_3$ modified by hexamethylenetetramine (13).

In the epoxidation of primary and secondary allylic alcohols catalyzed by a $TiO_2$–$SiO_2$ aerogel, high selectivities could be achieved in the presence of (basic) zeolite 4Å or $NaHCO_3$ as additives (8). Under the same conditions, epoxidation of alkyl-substituted cyclohexenols yielded epoxides only as minor products (<10% selectivity). We have recently reported (14) that unusually high selectivities can be achieved in the epoxidation of sensitive alkyl-substituted cyclohexenols in the presence of amine additives. Here we report a detailed study of the effect of amine additives on the epoxidation of 3-methyl-2-cyclohexen-1-ol. The possible extension of the application range of the method will be illustrated by the oxidation of other unsaturated compounds: isophorol, 2-cyclohexen-1-ol, cinnamylalcohol, 2-hexen-1-ol, and 2-hexene.

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0021-9517/99 $30.00

## 2. EXPERIMENTAL

### 2.1. *Materials*

3-Methyl-2-cyclohexen-1-ol (**1**) (Aldrich, 96%), 3,5,5-trimethyl-2-cyclohexen-1-ol (isophorol, Fluka, >95%), 2-cyclohexen-1-ol (Fluka, ca. 97%), *trans*-3-phenyl-2-propen-1-ol (cinnamyl alcohol, Fluka, ≥97%), and *trans*-2-hexen-1-ol (**8**) (Aldrich, 96%) were distilled prior to use. *Trans*-2-hexene (Fluka, ≥98%) was used as received. Ethylbenzene (Fluka, >99%), and toluene (Riedel-de Haën, >99.7) were distilled and stored over molecular sieve 4Å. Dodecane (Aldrich, >99%) was dried and stored over a molecular sieve 4Å. *Tert*-butylhydroperoxide (TBHP, Fluka, ca. 5.5 M solution in nonane, stored over molecular sieve 4Å) and the additives and reference materials were used as received. Molecular sieve 4Å (Chemie Uetikon) was activated overnight at 473 K in vacuum.

2,3-Epoxy-3-methyl-1-cyclohexanol (**2**), 2,3-epoxy-3,5,5-trimethyl-1-cyclohexanol, 2,3-epoxycyclohexanol, and 2,3-epoxyhexane were synthesized by oxidation with *m*-CPBA (15) and identified by $^1$H NMR and $^{13}$C NMR.

### 2.2. *Catalyst Preparation and Characterization*

The titania–silica aerogel containing 20 wt% $TiO_2$ was prepared using a sol–gel method. The solvent was semicontinuously extracted with supercritical $CO_2$ at 313 K and 24 MPa (low-temperature aerogel). The raw aerogel was calcined in air at 673 K for 5 h. Detailed descriptions of the synthesis and characterization of the aerogels by $N_2$-physisorption, X-ray diffraction, thermal analysis, XPS, and vibrational spectroscopy have been published earlier (3, 6, 16, 17). The X-ray amorphous material possessed a good Ti dispersion, high surface area ($S_{BET} = 680$ m$^2$/g), and a mesoporous structure (mean pore diameter, 9 nm).

### 2.3. *Epoxidation Procedure*

All reactions were conducted under argon to avoid the presence of oxygen and moisture. In the standard epoxidation procedure, 0.1 g catalyst was dried by heating to 473 K for 16 h in a 25-ml glass reactor fitted with magnetic stirring, thermometer, reflux condenser, and a septum for withdrawing samples. To the *in situ* dried catalyst were then added 10 mmol reactant, 0.5 ml internal standard (usually dodecane), and toluene (solvent). The reaction was started by adding 2.5 mmol TBHP in nonane (olefin : TBHP = 4/1 molar ratio) at 333 K. The total reaction volume was 10 ml. In most reactions two additives were also applied: 0.1 g activated molecular sieve 4Å and/or some amine (the amount used is given in mol% related to the reactant and will be indicated in the tables and figures).

Aliquots were removed after various time intervals, filtered, and analyzed by GC (HP-5890 equipped with a cool on-column inlet and an HP-FFAP capillary column). Side products were either identified with GC by comparison with authentic samples (3-methyl-2-cyclohexen-1-one) or by GC-MS and $^1$H- and $^{13}$C NMR. The internal standard method was used for quantitative analysis. Hydroperoxide conversion was determined by iodometric titration using a Metrohm 686 Titroprocessor.

Two different types of selectivities are used for characterization. Epoxide selectivity (related to the reactant consumed):

$$S_{C=C}\ (\%) = 100 \cdot [\mathbf{2}]/([\mathbf{1}]_0 - [\mathbf{1}]).$$

Peroxide selectivity (epoxide related to the peroxide consumed):

$$S_{TBHP}\ (\%) = 100 \cdot [\mathbf{2}]/([TBHP]_0 - [TBHP]).$$

The epoxide yield is referred to the amount of epoxide formed related to the initial TBHP concentration:

$$Y = 100 \cdot [\mathbf{2}]/[TBHP]_0.$$

The subscript 0 stands for initial values. Olefin conversion is given in mol% of the maximal attainable value (i.e., related to the peroxide).

### 2.4. *Decomposition of 2,3-Epoxy-3-Methylcyclohexanol (**2**)*

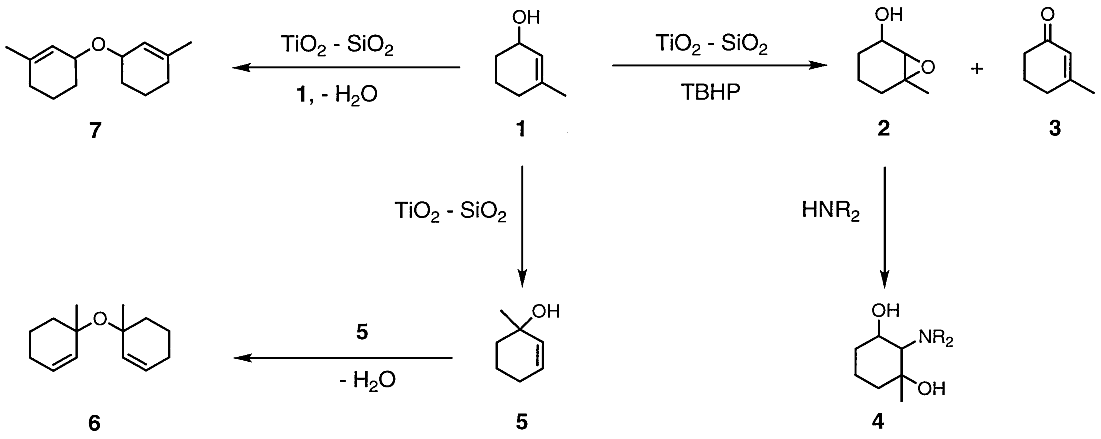
Catalyst (0.1 g, dried *in situ* at 473 K), 1.25 mmol **2**, 1.25 mmol TBHP, 8.75 mmol 2-hexanol (to mimic the presence of alcoholic reactant), 0.5 ml ethylbenzene, and 8 ml toluene were heated to 333 K. Depending on the reaction conditions, 0.1 g zeolite 4Å and/or 0.5 mmol 1-phenylethylamine were used as additives.

### 2.5. *Decomposition of Amine Modifiers*

Catalyst (0.1 g) was heated in an argon flow to 473 K for 16 h. Amine (5 mmol), 12.5 ml toluene, and 0.5 ml ethylbenzene (internal standard) were added and heated to 333 K, and the reaction started by introducing 12.5 mmol TBHP.

## 3. RESULTS

High olefin conversion (above 100% related to TBHP) and very low epoxide selectivity were characteristic of the epoxidation of 3-methyl-2-cyclohexen-1-ol (**1**) with TBHP and the aerogel (14). Further attempts by varying the reaction conditions (temperature, solvent) or addition of basic zeolite 4Å, did not lead to significant selectivity improvement. (Note that zeolite 4Å is widely used in homogeneous epoxidations catalyzed by Ti complexes to maintain dry conditions (18).) These preliminary experiments indicated that the main reason for the poor epoxide selectivity is the nonoxidative consumption of the reactant. A thorough



**SCHEME 1**

study of side reactions seemed to be inevitable before developing a better epoxidation procedure.

### 3.1. *Nature of Side Reactions during Epoxidation of* ***1***

A detailed picture of parallel and consecutive reactions during the epoxidation of **1** is shown in Scheme 1. The scheme includes only those products (**2**–**7**) which could be identified by GC-MS, $^1$H NMR, $^{13}$C NMR, two-dimensional NMR ($^1$H–$^{13}$C), and elemental analysis. Oligo- and polymerization of **1** (or any of the products) are not shown, though these reactions were often found to be dominant. Note that oligo- and polymers can block the active Ti site in the catalyst pores (19). It was proposed that catalyst drying and base additives can neutralize the acidic sites on the catalyst and thus prevent the acid-catalyzed formation of oligo- and polymers. When applying the standard procedure without any additive, or with zeolite 4Å, the epoxide (**2**) was only a minor product. The allylic alcohol **1** was rapidly converted in nonoxidative pathways, indicated by the high olefin conversion above 100% based on TBHP. Apparently the aerogel catalyzed the dehydration of **1** to **7** and the isomerization to **5**, followed by dehydration to **6**, more efficiently than the epoxidation to **2**. Under standard conditions and in the presence of zeolite 4Å, the selectivities to different products after 15 min (194% olefin conversion) were as follows: 3.5% **2**, 0.5% **3**, 24% **5**, 6% **6**, 18% **7**, and 48% nonvolatile products (mainly oligomers). Note that isomerization of **1** to **5** with a $Me_3SiOOSiMe_3$–$VO(acac)_2$ catalyst has been reported to proceed at room temperature (20).

It will be shown later that the acid-catalyzed side reactions leading to **5**, **6**, **7** and oligomers can be efficiently suppressed by amine additives. However, the presence of too high amounts of amines results in the formation of other by-products. Oxidation of the alcoholic functional group of **1** leading to the unsaturated ketone **3** became important, amounting to 45%. Primary and secondary amine additives (e.g., aniline and 1-phenylethylamine) react with the epoxide to yield **4**. The kinetics of the formation of various side products in the presence of amines will be discussed in Section 3.6.

### 3.2. *Epoxidation of* ***1*** *in the Presence of Various Amines*

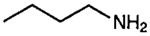
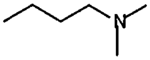
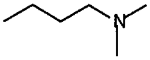
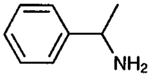
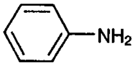
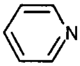
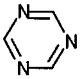
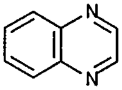
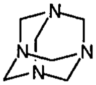
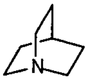
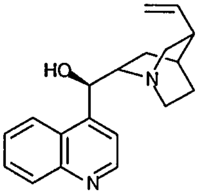
The important results of the epoxidation of **1** using different amines as additives are shown in Table 1. Amines decreased the conversion rate, indicated by the time required for 20% olefin conversion ($t_{20\%}$). In most cases, epoxidation was accelerated and the apparent rate of epoxide formation increased in the presence of amines. (The measured or apparent rate corresponds to the real rate of epoxide formation minus the rates of epoxide decomposition to byproducts). The undesired reactions of both the epoxide **2** and the allylic alcohol **1** could be suppressed by using small amounts of amine additives, resulting in striking selectivity enhancements with most of the amines tested. Note that with some amines (e.g., hexamethylenetetramine) deactivation of the catalyst was observed above 20% olefin conversion, likely due to the too high amine/**1** ratio (10 mol%). Interestingly, bulky compounds such as cinchonidine did not result in catalyst deactivation (blocking of the pores) when only 1 mol% of the amine was used.

There is no clear correlation between the structure of the amine additive and the diastereomeric ratio in the epoxide **2** (Table 1), though most of the amines which improved the epoxide selectivity (related to the olefin) increased the *cis/trans* ratio by ca. 5%.

It is clearly seen in Table 1 that a relation between basicity of the amine (p$K_a$) and epoxide selectivity is completely missing. For example, strongly basic primary amines can have a large (1-phenylethylamine) or only a small (butylamine) positive influence on the epoxide selectivity. The missing correlation between basicity and epoxidation selectivity may partly be due to the fact that p$K_a$ is determined in aqueous medium. Other reasons will be discussed later.

## TABLE 1

## Epoxidation of 3-Methyl-2-Cyclohexen-1-ol (1) with Different Amines as Modifiers[a]

| Modifier | $pK_a$[b] | $t_{20\%}$[c] (min) | Epoxide selectivity (%)[d] |  | Apparent rate of epoxide formation[e] ($mmol\ g^{-1}\ h^{-1}$) | Diastereomeric ratio (*cis* : *trans*) |
|---|---|---|---|---|---|---|
|  |  |  | $S_{C=C}$ | $S_{TBHP}$ |  |  |
| — | — | 0.85 | 3 | 35 | 6.6 | 89 : 11 |
|  | 10.77 | 36 | 9 | 19 | 1.2 | 94 : 6 |
|  | 10.2 | 160 | 94 | 32 | 5.6 | 94 : 6 |
|  | 10.2 | 5.3[f] | 99[f] | 100[f] | 40[f] | 93 : 7[f] |
|  | 9.35 | 45 | 88 | 65 | 7.6 | 94 : 6 |
|  | 4.63 | 1.2 | 3 | 89 | 5.9 | 89 : 11 |
|  | 5.25 | 15 | 60 | 69 | 12 | 93 : 7 |
|  | 0.65 | 12.5 | 96 | 92 | 21 | 94 : 6 |
|  | −1.7 | 9.2[g] | 95[g] | 92[g] | 26[g] | 94 : 6[g] |
|  | 0.56 | 1.6 | 13 | 49 | 14 | 91 : 9 |
|  | 8.87 | 300[h] | 21 | 6 | 1.8 | 95 : 5 |
|  | 10.9 | 25[f] | 79[f] | 89[f] | 11[f] | 94 : 6[f] |
|  | 8.4 | 18.4[f] | 50[f] | 81[f] | 9[f] | 90 : 10[f] |

[a] Standard reaction conditions; 10 mol% amine (based on **1**) and 0.1 g zeolite 4Å as additives.

[b] $pK_a$ values were taken from Refs. (27) and (28).

[c] Time needed for 20% conversion of **1** (from interpolation of the kinetic curves).

[d] Determined at 20% conversion.

[e] Actual amount of **2** expressed in mmol per unit amount of catalyst per unit time; determined at 15 min.

[f] 1 mol% amine (based on **1**) was used.

[g] Ethylbenzene was used as internal standard.

[h] 18% olefin conversion was reached in 300 min.

### *3.3. Influence of Amines on the Nonoxidative Conversion of **1***

As already mentioned in Section 3.1, amines can suppress the nonoxidative consumption of 3-methyl-2-cyclohexen-1-ol, including dehydration, isomerization, and oligomerization. The role of reaction components in these types of side reactions is shown in Fig. 1. Under standard reaction conditions (Fig. 1a) the reactant disappeared rapidly, whereas no reaction was observed when no aerogel was used (Fig. 1c). Conversion of **1** was even higher when zeolite 4Å was also present in the reaction mixture (Fig. 1b). The amounts of various products in the reaction mixture after 15 min are shown in Table 2 as an example.

In the absence of peroxide (but with zeolite 4Å) (Fig. 1d) the same observations were made as in the oxidation reaction with TBHP. Obviously, the nonoxidative conversion of **1** is catalyzed by the aerogel and also, to some extent, by the basic zeolite 4Å (mainly used to maintain dry conditions (18)). Addition of 5 mol% 1-phenylethylamine (Fig. 1e) stopped both oligomerization and ether formation, and no loss of **1** after 5 h reaction time was observed.

**TABLE 2**

**Product Composition after 15 min Epoxidation of 1**

| Changes related to the standard procedure | **1** converted[a] | **2** | **3** | **5** | **6** | **7** | nv[b] |
|---|---|---|---|---|---|---|---|
| — | 102 | 11 | 1 | 24 | 5 | 14 | 45 |
| No catalyst used | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Addition of 0.1 g zeolite 4Å | 194 | 3.5 | 1 | 24 | 6 | 18 | 47.5 |

*Note.* For conditions see Figs. 2a–2c. Data in %.

[a] Amount of **1** converted is related to $[TBHP]_0$.

[b] Nonvolatile products.

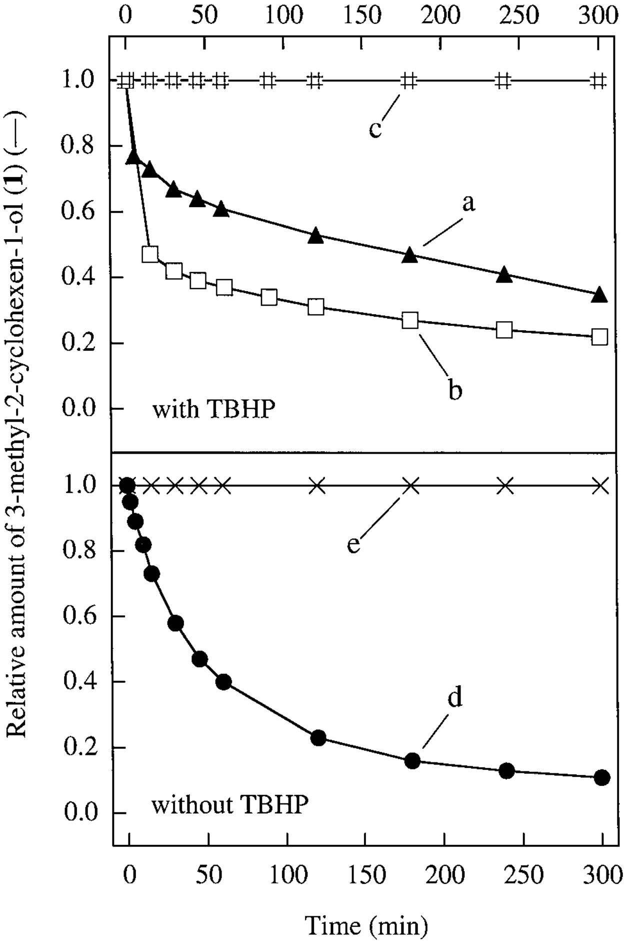


**FIG. 1.** Relative amount ($N/N_0$, where $N_0$ is initial amount) of 3-methyl-2-cyclohexen-1-ol (**1**) in the presence (top) and absence (bottom) of oxidant as a function of reaction time. Standard epoxidation conditions with the following modifications: (a) no modification; (b) addition of 0.1 g zeolite 4Å; (c) without catalyst; (d) addition of 0.1 g zeolite 4Å, no TBHP; (e) addition of 5 mol% 1-phenylethylamine, 0.1 g zeolite 4Å and 1.25 mmol *tert*-butanol (mimicking the presence of TBHP), no TBHP.

It seems that under standard reaction conditions the nonoxidative consumption of **1** is due to acid catalysis by the aerogel, and the addition of an appropriate amount of 1-phenylethylamine can hinder these reactions.

### *3.4. Influence of Amines on the Decomposition of Epoxide **2***

The low epoxide selectivity in the absence of amines was not only due to nonoxidative consumption of the reactant but also to decomposition of the epoxide formed. Decomposition of 2,3-epoxy-3-methylcyclohexanol (**2**) was studied using various additives (Fig. 2). Without any additive (standard conditions), continuous decomposition of the epoxide was effectively catalyzed by the aerogel. After 1 h reaction time 40% of the initial amount was converted. 1-Phenylethylamine suppressed the epoxide loss by a factor of 9 under otherwise identical conditions. When employing both amine and zeolite 4Å, no decomposition was observed. Interestingly, addition of zeolite 4Å could diminish the decomposition of epoxide, whereas the nonoxidative conversion of **1** was accelerated by this additive. Apparently, epoxide decomposition is catalyzed by the acidic aerogel, and both organic and inorganic bases can eliminate these acid-catalyzed side reactions. Zeolite 4Å also eliminates traces of water which can be formed by the homolytic decomposition of the alkylhydroperoxide or by the oxidative dehydrogenation of the alcoholic functional group. As a result, hydration of the aerogel and formation of new Brønsted sites (surface silanol groups) are prevented.

### *3.5. Stability of Amine Modifiers during Epoxidation*

The observations presented in Figs. 1 and 2 suggest that the positive effect of 1-phenylethylamine is connected to its basicity. On the contrary, no correlation between epoxide

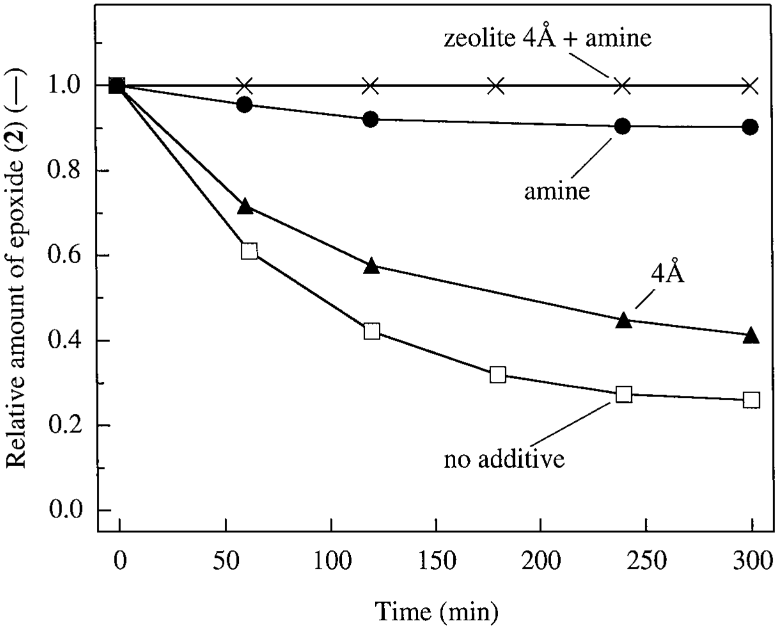


**FIG. 2.** Decomposition of 2,3-epoxy-3-methylcyclohexanol (**2**). Relative amount of **2** as a function of reaction time. Reaction conditions: 0.1 g catalyst, 1.25 mmol **2**, 8.75 mmol 2-hexanol, 1.25 mmol TBHP, 0.5 ml ethylbenzene (internal standard), 8 ml toluene; 333 K. Additives: (□) no additive, (▲) 0.1 g zeolite 4Å; (●) 0.5 mmol 1-phenylethylamine; (×) 0.1 g zeolite 4Å and 0.5 mmol 1-phenylethylamine.

selectivities and the p$K_a$ values of amine additives could be established, as discussed above. Besides the fact that p$K_a$ may not be suitable for characterizing the basicity of amines in a weakly polar medium, another feasible explanation for this contradiction is that some of the amines are not stable under the strongly oxidizing reaction conditions. In order to confirm this hypothesis, three different amines were chosen to study their resistance against oxidation under epoxidation conditions. The heteroaromatic compound triazine was one of the best modifier, affording high epoxide selectivities related to either the olefin or the peroxide (Table 1). Butylamine, a small primary alkylamine was the least efficient amine judged from the selectivities achieved at 20% olefin conversion. The aromatic amine aniline enhanced the peroxide efficiency but did not influence the epoxide selectivity related to the reactant olefin.

As shown in Fig. 3, aniline readily decomposed under oxidizing conditions similar to those of epoxidations, and after 15 min only 66% of the initial amount was left. On the other hand, butylamine and especially triazine were significantly more resistant against oxidation.

Stability of the amine additive itself may play an important role in the epoxidation of **1**. *Tert*-butylhydroperoxide can react with amines, giving products arising from $\alpha$-hydrogen abstraction or dealkylation by a homolytic process involving *tert*-butoxy- and *N*-oxide radicals (21). Formation of such radicals may explain the poor peroxide selectivities observed in the presence of, for example, butylamine and hexamethylenetetramine.

Note that in these experiments the amine concentration was 3–30 times higher than in most epoxidation reactions. The high amine concentration and the absence of a competing oxidizable substrate such as the allylic alcohol should increase the rate of amine decomposition. In other words, oxidative decomposition of the best modifiers *N*-heterocycles (e.g., triazine) or tertiary amines (e.g., $Me_2BuN$) during epoxidation may be minor.

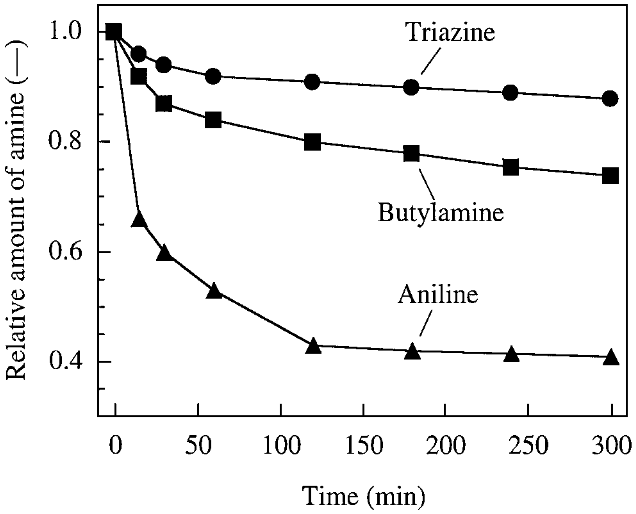


**FIG. 3.** Decomposition of triazine, butylamine, and aniline at 333 K. Relative amounts of amines as a function of reaction time. Detailed reaction conditions are given under Experimental.

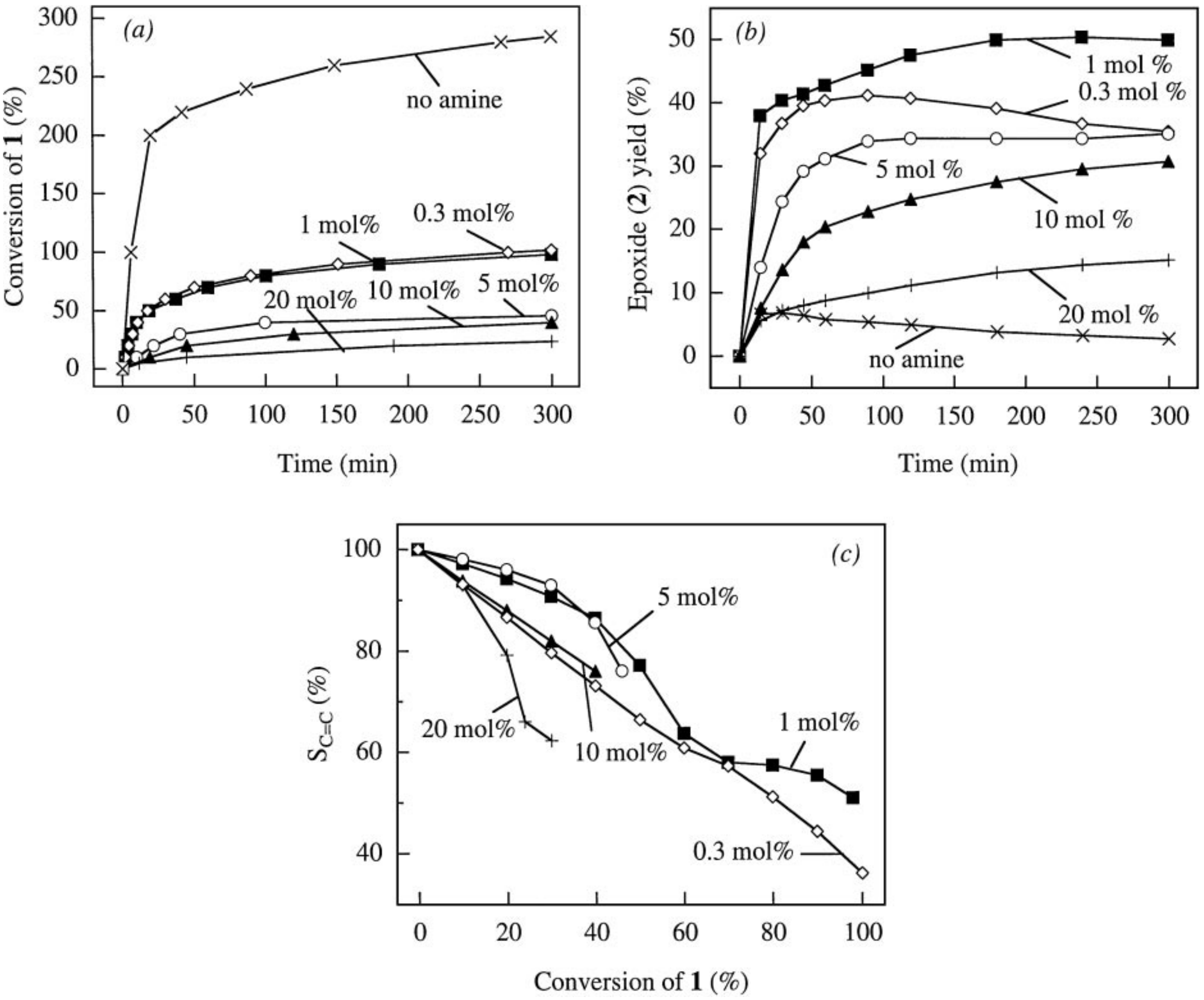


**FIG. 4.** Influence of the amount of 1-phenylethylamine as modifier on the conversion of **1** (a), epoxide (**2**) yield (b), and epoxide selectivity $S_{C=C}$ (c). Standard reaction conditions, in the presence of 0.1 g zeolite 4Å.

### *3.6. Influence of the Amount of Amine Modifier on the Epoxidation of **1***

The effect of amine concentration on the epoxidation of **1** under standard conditions was investigated using 1-phenylethylamine as an example. The kinetics of the reaction are shown in Figs. 4a–4c. The olefin conversion above 100% (related to TBHP) and the low epoxide yield in the absence of amine is indicative for the nonoxidative transformation of **1** (Figs. 4a and 4b). The apparent rate of epoxide formation was very low and after 30 min the decomposition became faster than its formation. With increasing amount of amine additive, the rate of olefin conversion decreased, whereas the rate of epoxide formation went through a maximum. Additive at 1 mol% was the optimum concerning the epoxide yield (Fig. 4b). Additive at 0.3 mol% enhanced the rate of epoxide formation as well, although this amount was not sufficient to suppress product decomposition, as indicated by the decay after 90 min. Due to the complex effect of amines on the rate of olefin conversion and epoxide formation and decomposition, the highest selectivity was obtained with 5 mol% amine below 30% conversion, but 1 mol% was the optimum at higher conversion (Fig. 4c).

Selectivities for the major side products as a function of the amount of additive are shown in Table 3. 1-Phenylethylamine suppressed the formation of the ethers **6** and **7**, isomerization of **1** to **5**, and oligomerization. However, increasing amount of amine led to oxidation of the alcoholic function of **1** to form the unsaturated ketone **3**. Epoxide ring opening and formation of the aminoalcohol **4** was observed when using at least 5 mol% 1-phenylethylamine.

A similar behavior was observed when the epoxidation of **1** was carried out in the presence of various amounts of triazine (14). In this case the highest epoxide yield of 56% was obtained with 5 mol% triazine. It seems that the optimum amount of amine varies markedly with structure and/or basicity of the additive.

**TABLE 3**

**Selectivities for the Side Products (3–7) and Oligomers as a Function of the Additive Amount**

| Amount of 1-phenylethylamine (mol%) | **3** | **4** | **5** | **6** | **7** | Oligomers |
|---|---|---|---|---|---|---|
| 0 | 2 | 0 | 15 | 5 | 20 | 54 |
| 0.3 | 3.5 | 0 | 6 | 1 | 5 | 50 |
| 1 | 3 | 0 | 1 | <1 | <1 | 45 |
| 5 | 11 | 7 | <1 | 0 | 1 | 4 |
| 10 | 15 | 11 | 1 | <1 | 3 | 0 |
| 20 | 28 | 18 | <1 | 0 | 3 | 0 |

*Note*. Standard reaction conditions, in the presence of 0.1 g zeolite 4Å, 5 h reaction time. Data in %.

### 3.7. *Epoxidation of Other Unsaturated Compounds in the Presence of Amine Modifier*

In order to explore the application range of amine additives in the epoxidation of allylic alcohols, the oxidation of some other reactants has been investigated in the presence and absence of 1-phenylethylamine. Oxidation of 3,5,5-trimethyl-2-cyclohexen-1-ol (isophorol) without amine additive at 363 K resulted in by-products mainly by nonoxidative reactions (as indicated by the conversion higher than 100%, related to TBHP), and only 10% epoxide selectivity was achieved (Table 4). 1-Phenylethylamine (1 mol%) suppressed these side reactions and the epoxide selectivities $S_{C=C}$ and $S_{TBHP}$ increased substantially.

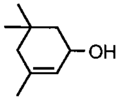
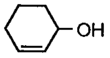
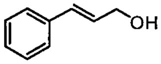
Epoxidation of cyclohexenol, bearing no substituent, was also investigated to reveal the role of alkyl substituents at the C=C double bond. In the absence of amine, dimerization of cyclohexenol to produce the corresponding ether analogous to **7** (Scheme 1) was the major side reaction. Addition of 1-phenylethylamine suppressed the dimerization and accelerated the epoxidation, leading to better epoxide selectivities $S_{C=C}$ and $S_{TBHP}$. Phenylethylamine improved the selectivities also in the epoxidation of cinnamyl alcohol, but $S_{C=C}$ and $S_{TBHP}$ were very low even in the presence of modifier (Table 4).

2-Hexen-1-ol (**8**) is moderately sensitive to acid-catalyzed side reactions under the epoxidation conditions, and it has been shown earlier (19) that addition of inorganic bases can significantly improve the epoxide selectivity $S_{C=C}$. Addition of 1-phenylethylamine lowered the reaction rate as compared to the standard reaction (Fig. 5). Note that some loss of activity of titania–silica or Ti-substituted zeolites is frequently observed upon addition of a base to the reaction mixture or after treating the catalysts with basic solutions (9, 11, 12). Application of low amine concentration in hexenol epoxidation suppressed the formation of oligomers, and epoxide ring opening by the reactant allylic alcohol yielding the ether-diol **11** (Scheme 2). As a result, the epoxide selectivity $S_{C=C}$ improved by 20–25% in the conversion range studied (Fig. 5). It is very likely that suppression of epoxide ring opening and oligomer formation with small amount of $N$-base is the result of reduced acidic character of the aerogel. A relatively high amine concentration (10 mol% based on the reactant) led to a rapid loss of epoxidation activity and a sharp decrease of $S_{C=C}$. Most of the initially formed epoxide underwent an addition reaction with the amine to produce the corresponding dihydroxy amine (**12**), as shown in Scheme 2.

In the epoxidation of 2-hexene, addition of 1-phenylethylamine lowered the initial reaction rate, but after 2 h the

**TABLE 4**

**Epoxidation of Some Cyclic Allylic Alcohols Using 1-Phenylethylamine as Modifier**[a]

| Reactant | Amine[b] (mol%) | Zeolite 4Å additive (g) | Conversion[c] (%) | $S_{C=C}$ (%) | $S_{TBHP}$ (%) | Diastereomeric ratio (*cis* : *trans*) |
|---|---|---|---|---|---|---|
|  | — | 0.5 | 221 | 10 | 30 | —[d] |
| | 1 | 0.5 | 72 | 58 | 51 | —[d] |
|  | — | — | 116[e] | 16[e] | 37[e] | 64 : 36[e] |
| | 1 | — | 64[e] | 63[e] | 51[e] | 74 : 26[e] |
|  | — | — | 73[f] | 6[f] | 7[f] | — |
| | 1 | — | 62 | 15 | 14 | — |

[a] Reaction conditions: 70 mg catalyst (dried *in situ* at 473 K); 20 mmol reactant; 5 mmol TBHP; 0.5 ml internal standard (ethylbenzene for the reactions without amine additive, dodecane for the others); toluene (solvent); total volume, 6 ml; 363 K; 1 h.

[b] Amount of additive is related to the reactant.

[c] Reactant conversion is related to TBHP (olefin : TBHP = 4 : 1).

[d] Diastereomers could not be separated by gas chromatography.

[e] Reaction conditions: 100 mg catalyst (dried *in situ* at 473 K for 1 h); 10 mmol 2-cyclohexen-1-ol; 2.5 mmol TBHP; 0.5 ml dodecan (internal standard); toluene (solvent); total volume, 10 ml; 363 K; 1 h.

[f] Dodecane was used as the internal standard.

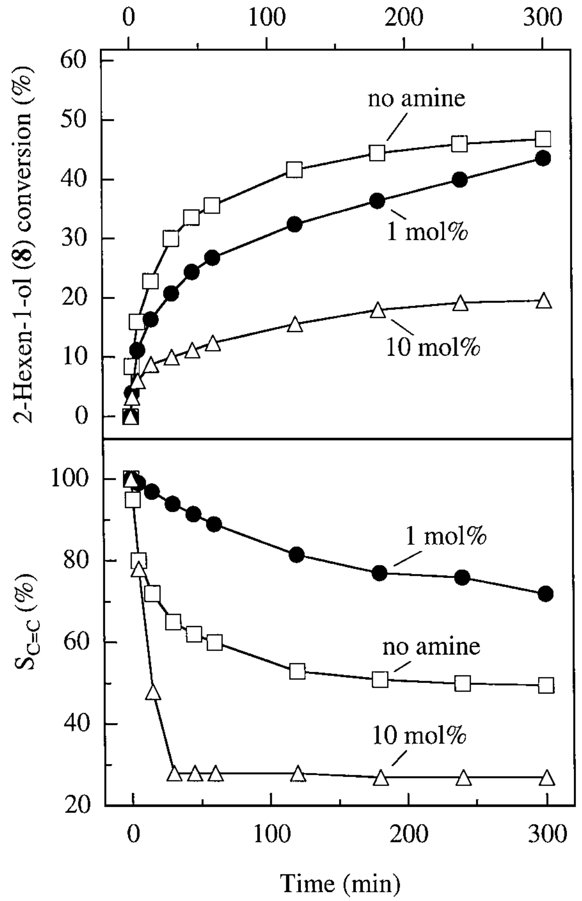


**FIG. 5.** Influence of 1-phenylethylamine as modifier on the conversion (top) and epoxide selectivity $S_{C=C}$ (bottom) in the epoxidation of 2-hexen-1-ol. Standard epoxidation conditions with the following modifications: (□) no amine, (●) 1 mol% 1-phenylethylamine, (△) 10 mol% 1-phenylethylamine.

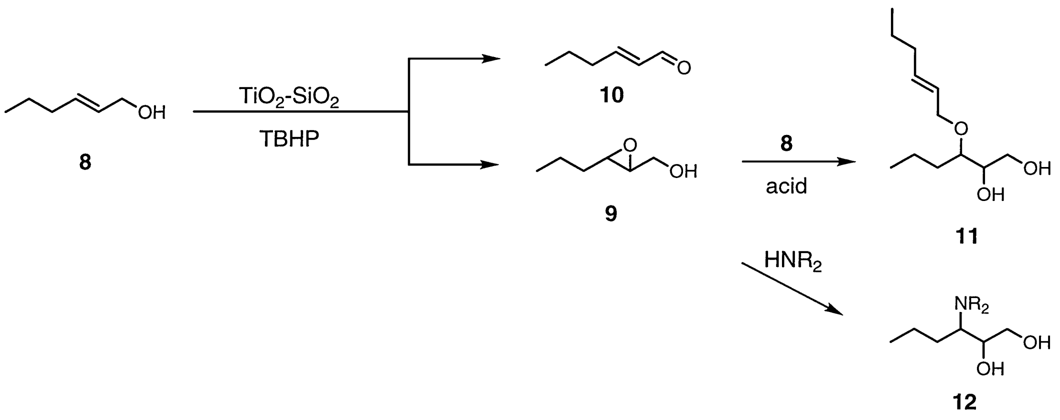
same olefin conversion (62%) was attained as without base (not shown here). This reaction was characterized by slow epoxide formation under standard conditions, resulting in poor epoxide selectivity, which could not be raised by amine addition.

## 4. DISCUSSION

An important result emerging from the experimental study is that selectivities in the epoxidation of various allylic alcohols can be improved by the addition of a small amount of an amine. The effect is most striking for cyclohexenols bearing an alkyl substituent at the C=C double bond and less pronounced for the open chain substrates 2-hexen-1-ol and cinnamyl alcohol.

The influence of amine modifiers on the performance of a 20 wt% $TiO_2$–$SiO_2$ aerogel was studied in the epoxidation of various linear and cyclic allylic alcohols and olefins. Under standard reaction conditions, epoxidation of 3-methyl-2-cyclohexen-1-ol (**1**) represented only a minor reaction and the reactant was rapidly converted to the isomeric allylic alcohol **5**, dimeric ethers **6** and **7**, and high-molecular-weight, nonvolatile substances. These undesired reactions were of nonoxidative nature as the amount of **1** consumed was higher than the initial amount of TBHP. Amine modifiers suppressed the acid-catalyzed side reactions and enhanced the rate of oxidation reactions. In the best case, the epoxide selectivity $S_{C=C}$ could be improved from 3 to 99% ($S_{TBHP}$ from 35 to 100%) at 20% conversion in the presence of only 1 mol% *N*,*N*-dimethylbutylamine. Too high amine concentration accelerated the oxidative dehydrogenation of the alcoholic functional group to form 3-methyl-2-cyclohexen-1-one (**3**). Likewise, epoxide ring opening became an important consecutive reaction with high modifier concentrations, due to the nucleophilic nature of amines.

An extension of the study to other allylic alcohols and olefins revealed that amines, even in low concentrations, reduce the rate of epoxidation and their positive influence on the epoxidation selectivity is limited to allylic alcohols. The scope of the successful application of amine modifiers seems to be determined by the nature of side reactions catalyzed by the titania–silica aerogel. As illustrated in Schemes 1 and 2, many of the side reactions of the reactant allylic alcohols and product epoxy-alcohols are catalyzed by acids. Three different types of acidic sites have been proposed to

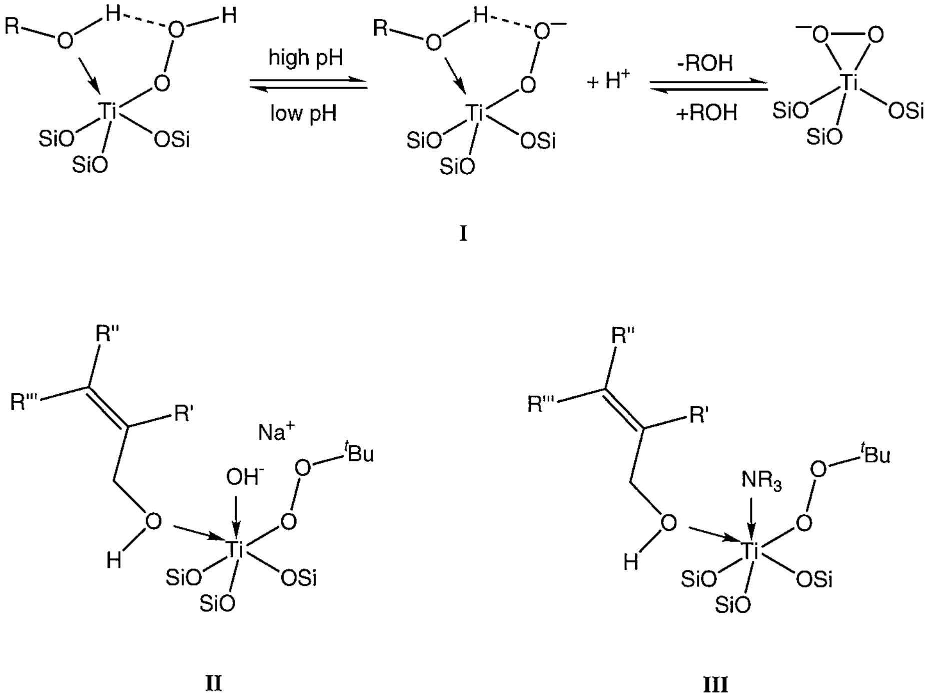


**SCHEME 2**

be present on the aerogel, which are probably involved in by-product formation: (i) atomically dispersed Ti(IV) in the silica matrix [Ti(OSi≡)$_4$] represents Lewis acid sites which are responsible for the high activity in alkene epoxidation (22); (ii) other Lewis acidic species are Ti(IV) atoms located in titania nanodomains (Ti connected via oxygen to Si and/or Ti atoms), which possess only moderate epoxidation activity (6); (iii) surface silanol groups which represent Brønsted acidic sites. Note that in epoxide decomposition the Ti–peroxo complex formed after addition of TBHP was found to be considerably more acidic than titania–silica (or TS-1) in the absence of TBHP (11, 23).

Suppression of side reactions is obviously due to neutralization of acidic sites on the catalyst by the amine additives. Upon addition of bases to TS-1 in epoxidations with $H_2O_2$, formation of a stable peroxo complex at the Ti sites has been proposed (**I** in Scheme 3) (24). The low reactivity of this species was attributed to its reduced electrophilicity caused by the negative charge. However, this mechanism involves abstraction of a proton from the peroxo complex formed with $H_2O_2$ and cannot be used to explain the effect of bases on the Ti complex formed with TBHP as oxidant. We propose that basic compounds, beside neutralization of Brønsted surface silanol groups, coordinate to the titanium active site and reduce its acidity by electron donation (structures **II** and **III**). This structure could also account for the previously reported positive effect of basic zeolite 4Å observed in epoxidation reactions catalyzed by the aerogel (19) (structure **II**, NaOH in very low concentration is the basic species). As a consequence of the suppression of acid-catalyzed side reactions, the apparent rate of epoxide formation increased considerably as shown in Table 1 and Fig. 4. The apparent rate of epoxide formation is the experimentally observable rate, i.e., the real rate of epoxide formation less the rate of epoxide decomposition. In fact, it is very unlikely that the real (intrinsic) rate of epoxide formation could be enhanced by suppressing the Lewis acidity of the Ti active site (22). We propose that the observed positive effect on activity is due to suppression of the (acid-catalyzed) oligomerization. High-molecular-weight oligomers can block the active site and the (narrow) pores, resulting in an apparent loss of epoxidation rate. The observed maximum in the (apparent) rate of epoxide formation as a function of amine concentration (Fig. 4b) is attributed to several counteracting effects of increasing amine concentration: lower intrinsic activity of the Ti–peroxo complex, suppressed oligomerization of reactant and product(s), suppressed dehydration and isomerization of the epoxide, enhanced rate of epoxide ring opening with the amine modifier, and accelerated oxidation of the –OH function (Schemes 1 and 2).

Hence, it is not astonishing that no simple correlation could be established between the basic strength of the amine and the selectivity enhancement in the epoxidation reaction. Besides, it has been found that some amines tested were not stable under the oxidizing reaction conditions. In these control experiments the amine concentration was 3–30 times higher than in most epoxidation reactions, and the absence of allylic alcohol could also accelerate the oxidative decomposition of amines. Still, the lower epoxide



SCHEME 3

selectivity $S_{\mathrm{TBHP}}$ observed in the presence of some amines (e.g., $BuNH_2$ and hexamethylenetetramine, Table 1) suggests that decomposition of these amines under reaction conditions cannot be neglected.

Steric effects may also contribute to the missing correlation between amine basicity and epoxide selectivity. The bulkiness of cinchonidine and quinoxaline, as compared to that of quinuclidine and pyrazine, respectively, may be the reason for their lower performance ($S_{\mathrm{C=C}}$ and $S_{\mathrm{TBHP}}$, Table 1). The small but significant increase of *cis*/*trans* ratio of the epoxide in the presence of efficient amine modifiers indicates that steric strain, exerted by the modifier as a new "ligand" of Ti, is not negligible (25, 26). The increase of *cis*/*trans* ratio by 5–10% (Tables 1 and 4) corroborates the feasibility of structure **III** in Scheme 3.

The real nature of Ti active sites in titania nanodomains (6), and the influence of amines on their activity and selectivity is largely unknown. However, the contribution of these sites to the overall performance of an appropriately prepared titania–silica aerogel is assumed to be small.

As concerns the Brønsted sites in titania–silica, deactivation of the surface silanol groups does not require strong bases. It was shown that treatment of the aerogel with weakly basic $NaN_3$, and even neutral NaCl, suppressed the acid-catalyzed isomerization reactions and resulted in significant selectivity improvement in the epoxidation of $\beta$-isophorone (11). A feasible explanation is that the inorganic salt, as the most polar compound of the reaction mixture, will adsorb preferentially on the polar surface groups ($\equiv$Si–OH) and prevent the interaction (acid-catalyzed side reaction) with the reactant or product.

## 5. CONCLUSIONS

The epoxide selectivity in the titania–silica catalyzed oxidation of 3-methyl-2-cyclohexen-1-ol was improved dramatically using small amounts of amine modifiers. The action of amines is the suppression of acid-catalyzed parallel and consecutive reactions which are otherwise dominant. A model is suggested for the interpretation of the interaction of allylic alcohol, alkylhydroperoxide, and basic additive with the active Ti site isolated by silanol groups. This model requires further catalytic and/or spectroscopic confirmation.

The scope of successful application of amine modifiers seems to be limited to the epoxidation of allylic alcohols, where the most striking effect was achieved in the oxidation of cyclohexenols bearing an alkyl substituent at the C=C double bond.

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