The Mechanism of the Double Bond Cleavage in the Titanium Zeolite-Catalyzed Oxidation of α-Methylstyrene by Hydrogen Peroxide: The β-Hydroperoxy Alcohol as Intermediate

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It is unequivocally shown that acetophenone, an oxidation product in the titanium zeolite-catalyzed oxidation of α-methylstyrene, derives from 2-hydroperoxy-2-phenyl-1-propanol as intermediate, which was detected and isolated in this reaction for the first time.

Incorporation of transition metals by isomorphous substitution into the framework of zeolites and related molecular sieves has greatly expanded the possibilities for the use of selective oxidation catalysts in the manufacture of bulk as well as fine chemicals[1]. The first example of the so-called "redox molecular" sieves was the Ti-silicalite (TS-1) catalyst synthesized by Enichem workers[2]. TS-1 was shown to be very active and selective in the oxidation of a large number of substrates with H_2O_2 under mild conditions, provided that the molecules could enter the relatively small pores (ca. 5.5 Å) of the zeolite[3]. An important step forward in this field was the synthesis of the first large-pore Ti-zeolite, namely Ti-beta[4]. The benefits of the larger pores were manifested in the oxidation of bulkier substrates (branched and cyclic alkanes and alkenes) with hydrogen peroxide, and also in the possibility of using hydroperoxides as the oxygen source[5].

Recently, TS-1 has been shown to catalyze the epoxidation of styrene in dilute H_2O_2 solution[6]. During this reaction a relatively high yield of benzaldehyde (ca. 10–20% depending on solvent and reaction conditions) is formed by oxidative cleavage of the double bond. The extent of oxidative cleavage was even higher for α-methylstyrene with H_2O_2 under TS-1 and TS-2 catalysis[7], and acetophenone was produced in a yield of 50–65%. It is remarkable that despite the scientific and practical interest of Ti-zeolite catalysts, the detailed mechanism of epoxidation is not well known and the reaction intermediates remain mostly undefined.

We report here on the Ti-beta-catalyzed oxidation of α-methylstyrene and, by providing the first direct experimental evidence for the intermediate involved in the cleavage reaction, delineate the reaction mechanism. The intermediate is a hydroperoxy alcohol, which we have isolated from the reaction mixture and synthesized independently by a known literature procedure[8].

In acetonitrile, with Ti-beta, a mixture of 2-hydroperoxy-2-phenyl-1-propanol (**3a**), 2-phenyl-1,2-propanediol (**3b**), 2-phenylpropanal (**3c**) and the cleavage product acetophenone (**4**) is obtained (Scheme 1; entry 1, Table 1). The same products, but in different ratios and at lower yields, are observed when other titanium-containing zeolites are used, i.e. Ti-beta-Na (entry 2, Table 1) or TS-1 (entry 3, Table 1). The formation of various products and several control experiments in the reaction of the alkene **1** or the epoxide **2a** in different zeolites are depicted in Scheme 2. When the authentic epoxide **2a** was exposed to the oxidation conditions, the products were the same as those obtained from direct oxidation of substrate **1** (compare entries 1 in Tables 1 and 2). In the presence of water, the epoxide **2a** is hydrolyzed to the diol **3b** (conditions j, Scheme 2; entry 4, Table 2), which then persists in the acidic reaction medium and does not suffer C–C cleavage to acetophenone (**4**) or rearrange to the aldehyde **3c** (conditions l, Scheme 2). Epoxide opening also occurs with the more nucleophilic hydrogen peroxide to give the β-hydroperoxy alcohol **3a** (conditions d, Scheme 2), which can be isolated from the reaction mixture by column chromatography (see experimental part) after a reaction time of 2 h. Since the thermally labile hydroperoxy alcohol **3a** decomposes on attempted GC or GC-MS analysis into acetophenone (conditions e, Scheme 2), the reaction mixture was first treated with PPh_3 to reduce **3a** to its diol **3b** (conditions k, Scheme 2) prior to GC analysis. Even in the absence of any nucleo-

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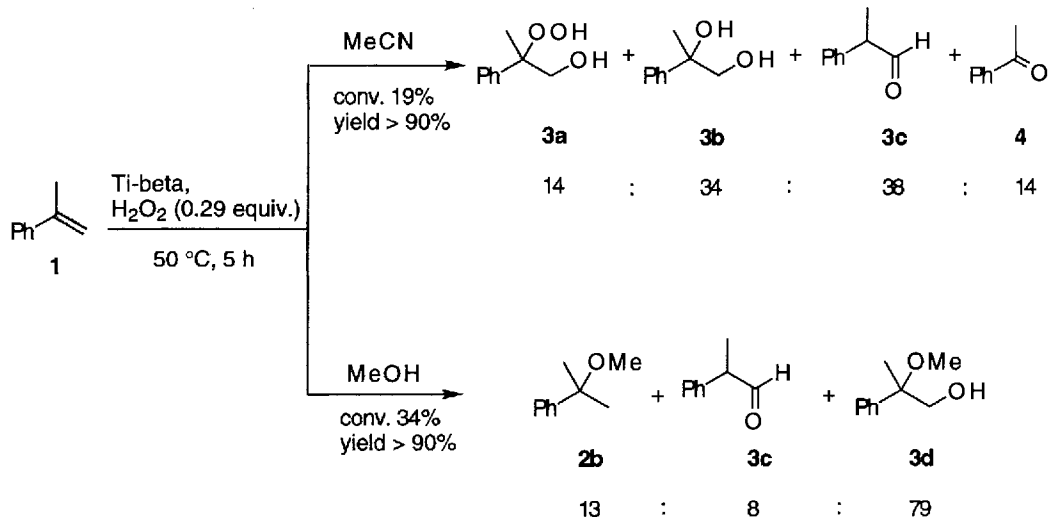
Scheme 1. Ti-Beta-catalyzed oxidation of α-methylstyrene



philes, the epoxide **2a** is labile in the presence of the catalyst and is rearranged completely within 5 h to the aldehyde **3c** (conditions i, Scheme 2; entry 5, Table 2). Moreover, under the oxidation conditions of the styrene **1** with Ti-beta (conditions a, Scheme 2), the cleavage-product acetophenone (**4**) is formed from the epoxide **2a** by Ti-beta-Na catalysis (conditions b, Scheme 2; entry 2, Table 2) as well as by the purely acidic beta-H catalyst (conditions c, Scheme 2; entry 3, Table 2).

Table 1. Product distribution in the oxidation of α-methylstyrene (**1**)

					Product distribution[a,b]				
Entry	Zeolite	Medium	Conv.[%][b]	**2b**	**3a**[c]	**3b**	**3c**	**3d**	**4**
1	Ti-beta	$MeCN/H_2O_2$	19		14	34	38		14
2	Ti-beta-Na	$MeCN/H_2O_2$	9		26	14	40		20
3	TS-1	$MeCN/H_2O_2$	4		23	14	27		36
4	Ti-beta	$MeOH/H_2O_2$	34	13			8	79	
5	Ti-beta	MeOH	2	100					

[a] Relative yields normalized to 100%. – [b] Determined by GC analysis, error ±5% of the stated value. – [c] Determined by GC analysis after reduction by PPh_3.

In contrast, in methanol (Scheme 1; entry 4, Table 1), the alcoholysis-product 2-methoxy-2-phenylpropanol (**3d**) was the major component (79%), together with small amounts of aldehyde **3c** (8%) and ether **2b** (13%). Indeed, the epoxide **2a** is ring-opened efficiently by methanol to give the ether **3d** (conditions h, Scheme 2, entry 6, Table 2). As a nonoxidation by-product of this reaction, methanol is also added in low yield to the substrate to give the ether **2b** (conditions g, Scheme 2; entry 5, Table 1).

Let us now mechanistically interpret and compare the Ti-beta-catalyzed oxidations of α-methylstyrene (**1**) in acetonitrile and methanol. In acetonitrile, under the reaction conditions, the labile primary oxidation product, 2-methyl-2-phenyloxirane (**2a**), either adds hydrogen peroxide or water to afford the hydroperoxy alcohol **3a** or the diol **3b**, respectively, or it rearranges to the aldehyde **3c** (conditions d, i and j, Scheme 2). The formation of the hydroperoxy alcohol **3a** can be catalyzed by both the Lewis acidic titanium sites, which are the only catalytically active species in Ti-beta-Na and TS-1 (entries 2 and 3, Table 1), and by the Brønsted acidic sites (Si–OH–Al) of beta-H (entry 3, Table 2). In Ti-beta, which possesses both titanium sites and Brønsted-acidic Si–OH–Al sites, the two types of acidity act synergistically. Acetophenone (**4**) is subsequently produced by Grob fragmentation of the β-hydroperoxy alcohol **3a**, a reaction which has been reported in the literature to proceed under basic[9] and acidic conditions[8b], and at elevated temperatures[10]. Control experiments have confirmed that the hydroperoxide **3a** is efficiently decomposed into acetophenone when it is exposed to aqueous hydrochloric acid or to $Ti(OiPr)_4$ in $CDCl_3$ (conditions f, Scheme 2). This confirms that both aqueous acidic conditions and the Lewis acidity of the Ti sites are effective in facilitating the fragmentation reaction of the hydroperoxy alcohol **3a** into acetophenone (**4**).

When methanol is used as solvent, the fragmentation to acetophenone is suppressed by solvolysis of the epoxide to the stable ether **3d**. Consequently, hydroperoxy alcohol **3a** is not formed and no cleavage to acetophenone is observed.

In summary, we have confirmed that 2-methyl-2-phenyloxirane (**2a**) is the primary product in the oxidation of α-methylstyrene with hydrogen peroxide with catalysis by Ti-containing zeolites. However, in acetonitrile, the epoxide **2a** is ring-opened by hydrogen peroxide to the hydroperoxide **3a**, which is responsible for acetophenone formation by Grob fragmentation. Both the nucleophilic ring opening reaction and the fragmentation process are catalyzed by Lewis acidic titanium as well as Brønsted acidic Si–OH–Al sites.

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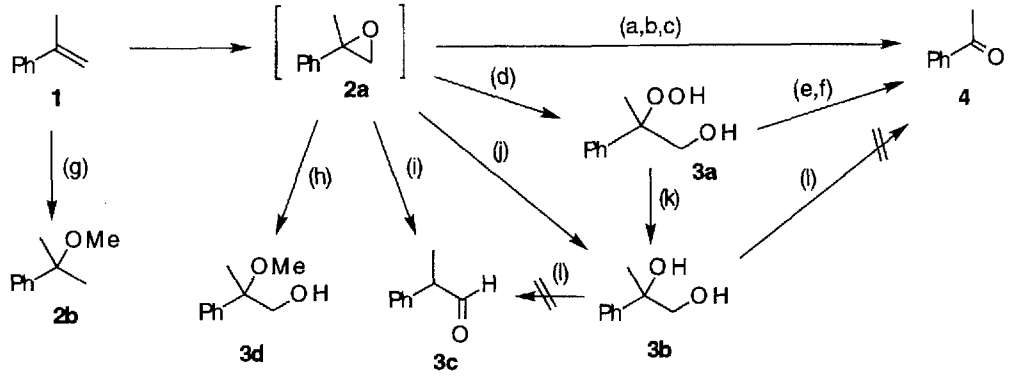
Scheme 2. Control experiments for the Ti-beta-catalyzed epoxidation of α-methylstyrene



(a)1. Ti-beta, H_2O_2, MeCN, 2. 250 °C (GC injector); (b) 1. Ti-beta-Na, H_2O_2, MeCN, 2. 250 °C (GC injector); (c) 1. beta-H, H_2O_2, MeCN, 2. 250 °C (GC injector); (d) Ti-beta, H_2O_2, MeCN; (e) 250 °C (GC injector); (f) DCl, D_2O, $CDCl_3$ or $Ti(OiPr)_4$, $CDCl_3$; (g) Ti-beta, MeOH; (h) Ti-beta, MeOH; (i) Ti-beta, MeCN; (j) Ti-beta, H_2O, MeCN; (k) PPh_3, MeCN; (l) Ti-beta, H_2O_2, MeCN;

Table 2. Product distribution in the control experiments with the epoxide **2a** and different zeolites as catalyst

				Product distribution[a,b]				
Entry	Zeolite	Medium	Conv.[%][b]	3b	3c	3d	4[c]	other
1	Ti-beta	$MeCN/H_2O_2$	>95	23	61		16	
2	Ti-beta-Na	$MeCN/H_2O_2$	>95	19	58		18	6[d]
3	beta-H	$MeCN/H_2O_2$	>95	39	47		8	6
4	Ti-beta	$MeCN/H_2O$	>95	23	77			
5	Ti-beta	MeCN	>95	5	95			
6	Ti-beta	MeOH	>95			>95		

[a] Relative yields normalized to 100%. – [b] Determined by GC analysis, error ±2% of the stated value. – [c] Some of the acetophenone (**4**) arises from decomposition of the hydroperoxide **3a**. – [d] 2-Phenylpropenol.

Experimental

Ti-beta (4 wt% TiO_2, Si/Al = 140) was synthesized as described in the literature[11] by using tetraethyl orthotitanate (TEOTi) and Aerosil (Degussa) as Ti and Si sources. The crystallization was carried out in teflon-lined autoclaves at 135 °C and 60 rpm. After crystallization, the solid was filtered, washed, dried at 80 °C and calcined at 580 °C for 5 h. The IR spectrum of the resultant sample exhibited the 960 cm^{-1} band, while a large concentration of external (3736 cm^{-1}) and internal (3530 cm^{-1}) silanol groups were observed in the OH region. The DRS UV-Vis spectrum showed bands only in the 205–230 nm range, attributable to framework Ti atoms with four- to sixfold coordination. The average crystallite size ranged from 0.1 to 0.2 μm.

The epoxidations were carried out in acetonitrile or methanol solution at 50 °C. α-Methylstyrene (17.5 mmol) and 35 wt% aqueous hydrogen peroxide (5.08 mmol, 0.29 equiv.) were dissolved in 15 ml solvent and heated to 50 °C. Ti-beta (100 mg) catalyst was added and the mixture stirred for 5 h. The reaction progress was monitored by GC and/or NMR (Varian, 300 MHz) analysis; for the latter the solvent was evaporated.

By following the above procedure (in 10 ml of acetonitrile, 2 h reaction time), 448 mg (2.66 mmol, 31%) of **3a** was obtained from 2-methyl-2-phenyloxirane (1.16 g, 8.64 mmol) and hydrogen peroxide (2.75 g, 8.65 mmol) after column chromatography (silica gel, 2:2:1 mixture of $CH_2Cl_2/Et_2O/n\text{-}C_6H_{14}$ as eluent, $R_f = 0.47$)[9].

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