Epoxidation of Lower Olefins with Hydrogen Peroxide and Titanium Silicalite

MARIO G. CLERICI[1] AND PATRIZIA INGALLINA

Eniricerche SpA, Via Maritano 26, I-20097 San Donato Milanese, Milano, Italy

The epoxidation of lower olefins, catalysed by titanium silicalite (TS-1) under mild conditions, is reported. The reaction may be performed at near room temperature, in dilute alcoholic or aqueous solutions of hydrogen peroxide. In methanol C_4–C_8 linear olefins, allyl chloride, and allyl alcohol show fast reaction rates and high selectivities (72–97% on H_2O_2). The solvolysis of the oxirane ring and the oxidation of the solvent are the main side reactions. Yields and kinetics are decreased by increasing the chain length or the cross-section of the olefin (n-C_n > n-C_{n-1}, 1-hexene $\gg$ cyclohexene), by electron-withdrawing substituents (1-butene > allyl chloride > allyl alcohol), and by solvents in the order methanol > ethanol > t-butanol. The rate of reaction also depends on the position and steric configuration of the double bond and on the branching, as a result of inductive and shape selectivity effects: *trans* 2-butene < iso-butene < 1-butene < *cis* 2-butene, 2-methyl-1-butene < 1-pentene, and 3-methyl-1-butene < 2-methyl-1-butene < 2-methyl-2-butene. The epoxidation occurs with retention of configuration. Basic compounds at low concentration do not slow the kinetics, but do improve significantly the yields, up to 97% in the epoxidation of 1-butene. At higher concentrations, TS-1 activity is decreased and eventually inhibited by bases. No effect on kinetics is exerted by tetrapropylammonium hydroxide. Catalytic activity is improved by acids. A heterolytic peracid-like mechanism is envisaged in the oxygen-transfer step. A five-membered cyclic structure, formed by a titanium hydroperoxo moiety Ti–OOH, and a protic molecule ROH at Ti sites, is proposed as the active species. © 1993 Academic Press, Inc.

INTRODUCTION

Hydrogen peroxide as well as organic hydroperoxides are relatively poor oxidants, in the absence of radical initiators or other specific reagents. Only strong nucleophiles, such as several phosphorus, nitrogen, and sulfur compounds, are readily oxidised under mild conditions. No reaction occurs with alkenes, unless a co-reagent suited to produce electrophilic intermediates, such as peracids and metal peroxo complexes, is used (*1*).

Early discovery concerned the epoxidation of olefins with percarboxylic acids, which are conveniently prepared by the reaction of carboxylic acids with hydrogen peroxide (*2*). Metal-catalysed epoxidations with organic hydroperoxides were even

more successful (*3*). Several studies have been published since the first reports, by Hawkins in 1950 (*4*) and by Indictor and Brill some years later (*5*). A commercial process for the manufacture of propylene oxide was rapidly developed by Halcon (*6*). Meanwhile, metal-catalysed epoxidations with hydrogen peroxide met with little success. Both slow rates and competing side reactions, such as the homolytic decomposition of the oxidant and the solvolysis of the oxirane ring, usually resulted in poor yields (*3*). The only exceptions of note were the epoxidations of α,β-unsaturated alcohols and acids, catalysed by titanium and tungsten complexes, respectively, which occurred with high selectivity (*7–9*). A major result has been achieved recently with titanium silicalite (TS-1), a new efficient epoxidation catalyst (*10*). Almost quantitative yields of propylene oxide are produced at

[1] To whom correspondence should be addressed.

near room temperature, by dilute methanol solutions of hydrogen peroxide (*11*). Preliminary accounts on C_4 olefins have also been given (*12, 13*).

Most of the detailed mechanistic proposals in the literature envisage peracid-like mechanisms, in which the active epoxidizing species acts as an electrophile. WO_3/H_2O_2 (*14–16*), CH_3CN/H_2O_2 (*17*), CF_3COCF_3/H_2O_2 (*3, 18*), M/ROOH (M = Group IV–VI transition metal complex) (*19, 20*), $BO_2R/ROOH$ (*21*), belong to this category. Common features shown by all these reagents are heterolytic mechanism, stereospecificity, and high yields to epoxide (often in the range 80–95% on the oxidant).

Homolytic epoxidations have also been reported. These are nonselective, normally yielding a mixture of products, as a result of allylic oxidation of the olefin and of further reactions of the oxirane ring. They also lack stereospecificity. The vanadium peroxo complexes described by Mimoun *et al.* are typical examples (*22*). These are also worth mentioning for their ability to hydroxylate both aliphatic and aromatic C–H bonds, under mild conditions.

Few mechanistic details are as yet available for the epoxidations catalysed by TS-1. Preliminary results on C_3–C_4 olefins (*11, 13*) and peracid-like structure of the species formed by hydrogen peroxide at titanium sites (*23*) suggest a heterolytic pathway. On the other hand, we have shown that in the oxyfunctionalization of alkanes, the H-abstraction step is mediated by a titanium peroxo species having homolytic character (*24*). One may speculate whether the same species is also involved in the epoxidation of the double bond.

The above considerations led to the conclusion that further investigation was needed in order to obtain more insight into the mechanistic details of the reaction. With this in mind, we have now examined the epoxidation of a variety of olefins, which are particularly suited to provide information on the selectivity and on electronic and steric effects of the reaction.

EXPERIMENTAL

The spectroscopic characterisation of TS-1 and the analytical procedures have been described elsewhere (*11, 23, 25*).

Materials

Methanol, ethanol, and *t*-butyl alcohol (C. Erba, RPE) were distilled and stored under nitrogen over 3A and 4A molecular sieves. 1-Pentene and C_6–C_8 olefins (Fluka, purum), and allyl chloride and allyl alcohol (Merck) were similarly purified. C_4 and branched C_5 olefins (Fluka, purum), aqueous tetrapropylammonium hydroxide (29.6 wt%, from EniChem Synthesis), GLC internal standards, and authentic samples of epoxides were used as received. Hydrogen peroxide (33% wt/vol) and *t*-butyl hydroperoxide (TBHP, 80% aqueous solution) were obtained from C. Erba. Anhydrous LiCl, NH_4F, $CH_3CO_2Li \cdot 1/3H_2O$, CH_3COOH, 40% HF, and 37% HCl were all reagent grade. TS-1 was prepared according to the literature (TiO_2 2.8 wt%, SiO_2/TiO_2 molar ratio 46, 0.1–0.3 μm crystallite size) (*11*).

Epoxidation of 1-Butene

A typical procedure was carried out as follows: 50 ml of a stock solution of 1-butene in methanol (0.938 *M*), 2.0 ml of hydrogen peroxide in methanol (2.57 *M*), and 0.377 g of benzene were charged into a 75-ml-capacity glass reactor, fitted with a nitrogen inlet, a thermometer, a serum cap, and a magnetic stirrer. An outer jacket was also provided in the reactor, through which a water/glycol mixture at -5 ± 0.1°C could be circulated. The reaction was started by adding 0.323 g of TS-1 under vigorous stirring. Aliquots were removed at various time intervals and analysed by iodometric titration and gas chromatography (Porapak PS, 6' $\times$ 1/8", 175°C).

Epoxidation of C_5–C_8 Olefins, Allyl Chloride, and Allyl Alcohol

In a typical run, 1-pentene (3.512 g) and MTBE (0.272 g) were weighed into a 50-ml

TABLE 1

Epoxidation of C_5–C_8 Olefins, Allyl Chloride, and Allyl Alcohol[a]

n	Olefin	$[H_2O_2]_0$ (M)	T (°C)	t (min)	H_2O_2 (conv. %)	Selectivity (% on H_2O_2)	$t_{1/2}$
1	1-Pentene	0.18	25	60	94	91	5
2	1-Hexene	0.18	25	70	88	90	8
3	1-Hexene[b]	0.18	25	70	68	90	14
4	Cyclohexene	0.18	25	90	9	[c]	—
5	1-Octene	0.17	45	45	81	91	5
6	Allyl chloride	0.18	45	30	98	92	7
7	Allyl alcohol	0.18	45	35	81	72	16
8	Allyl alcohol[d]	0.14	26	180	89	[c]	70

[a] The general procedure is given in the Experimental section. Olefin, 0.90 M; TS-1, 6.2 g/liter; solvent, methanol; $t_{1/2}$ is the time required for 50% H_2O_2 conversion.

[b] [1-Hexene] 0.18 M.

[c] Not determined.

[d] TS-1 4.0 g/liter.

volumetric flask, then methanol was added to the mark. An amount of 45.0 ml of this solution and 5.0 ml of hydrogen peroxide in methanol (1.80 M) were charged into the 75-ml jacketed glass reactor. TS-1 (0.310 g) was added at 25.0°C, under vigorous stirring. Analyses were performed by iodometric titration and GLC on Porapak PS.

Chlorobenzene, 1,2-dimethoxyethane, and MTBE were used as GLC internal standards for allyl chloride, allyl alcohol, and for all other olefins, respectively. GLC analyses were performed on Porapak PS and on PONA (1-hexene). Results are illustrated in Table 1.

The reactions at 0°C, those of 1-pentene in methanol and t-butylhydroperoxide (TBHP), in ethanol, and t-butanol were similarly carried out.

Competition Kinetics

A typical procedure was carried out by dissolving, under nitrogen and at low temperature, the olefins in methanol to the required concentrations. Known amounts of these solutions, aqueous 33% hydrogen peroxide, and GLC internal standard (benzene or MTBE) were charged into the 75-ml jacketed glass reactor, cooled to −5°C. An aliquot (2.0 ml) was withdrawn and titrated for hydrogen peroxide. The reaction was started by adding titanium silicalite, under vigorous stirring. Aliquots were withdrawn with a syringe at various time intervals (0.5 ml), quenched with 0.1 ml aqueous CH_3CO_2Li (2.2 M), and cooled to −78°C until GLC analyses were made. The reaction was ended when hydrolysis products were detected in the reaction mixture. GLC analyses were generally performed on Porapak PS. The $epoxide_1$/$epoxide_2$ ratio remained constant, within the experimental errors, during the reaction. Relative rates of epoxidation were determined by the formula (26)

$$\frac{v_1}{v_2} = \frac{\ln([A]_0/[A]_t)}{\ln([B]_0/[B]_t)},$$

where $[A]_0$, $[A]_t$ and $[B]_0$, $[B]_t$ are the concentrations of $olefin_1$ and $olefin_2$, respectively, at the beginning and at the time the sampling was made. Results are illustrated in Table 2. Each v_1/v_2 ratio is an average value of 7–10 aliquot analyses, taken at different reaction times, in the same run.

Response factors of branched C_5 olefins epoxides were assumed to be equal to that

TABLE 2

Competitive Epoxidation of C_4 Olefins and 1-Pentene. Experimental Conditions and Results[a]

n	Olefin$_1$ (M)	Olefin$_2$ (M)	[H$_2$O$_2$] (M)	t (min)	H$_2$O$_2$ (conv.%)	v_1/v_2
1	cis 2-Butene (0.212)	Isobutene (0.505)	0.28	180	47	3.4 ± 0.2
2	cis 2-Butene (0.678)	Isobutene (0.737)	0.083	70	72	3.3 ± 0.1
3	1-Butene (0.370)	Isobutene (0.454)	0.16	60	54	1.45 ± 0.1
4	1-Butene (0.541)	Isobutene (0.859)	0.084	40	53	1.4 ± 0.1
5	cis 2-Butene (0.108)	trans 2-Butene (0.612)	0.15	80	54	16.2 ± 0.3
6	cis 2-Butene (0.711)	1-Butene (0.704)	0.085	70	89	2.7 ± 0.1
7	Isobutene (0.119)	trans 2-Butene (0.553)	0.096	45	50	4.7 ± 0.2
8	1-Butene (0.648)	1-Pentene (0.350)	0.11	80	74	1.7 ± 0.1
9	1-Pentene (0.240)	trans 2-Butene (0.355)	0.12	80	63	3.4 ± 0.1

[a] The general procedure is given in the Experimental section. Temp., −5°C; TS-1, 6.0 g/liter; solvent, methanol.

of 1,2-epoxypentane. v_1/v_2 ratios are shown in Table 3.

Epoxidation of cis 2-Butene and trans 2-Butene in Methanol

Method A. The procedure for 1-butene was adopted for $T \leq 0°C$. GLC analyses (benzene as internal standard) were performed on Porapak PS, 6' × 1/8″, at 185°C. Cis and trans 2,3-epoxybutane, threo and erythro 2-hydroxy-3-methoxybutane showed well resolved chromatographic peaks. Solvolysis was only detected in the epoxidation of cis olefin, at over 80% H$_2$O$_2$ conversion.

Method B. A different procedure was adopted for $T \geq 50°C$. Hydrogen peroxide in methanol (40 ml, 0.08 M) and TS-1 (0.20 g) were charged into a 300-ml-volume glass pressure vessel, fitted with an inlet for gaseous olefin, an outlet for liquid sampling, and a thermocouple. The slurry was heated at 50°C, cis 2-butene was charged at approximately constant pressure (103 kPa), and stirring was continued for further 10 min. Cis 2,3-epoxybutane and threo 2-hydroxy-3-methoxybutane were produced in a 3:1 ratio. To the limits of detection, trans 2,3-epoxybutane and erythro 2-hydroxy-3-methoxybutane were not observed among the by-products, present as trace amounts in the reaction mixture (the latter by-products were also formed in the solvolysis of cis 2,3-epoxybutane, under analogous conditions).

TABLE 3

Relative Rates of Epoxidation of Branched C_5 Olefins vs trans 2-Butene. Experimental Conditions and Results[a]

n	Olefin$_1$ (M)	Olefin$_2$ (M)	t (min)	H$_2$O$_2$ (conv.%)	v_1/v_2
1	trans 2-Butene (0.75)	2-Methyl-2-butene (0.55)	70	44	1.1 ± 0.1
2	trans 2-Butene (0.93)	2-Methyl-1-butene (0.77)	140	49	4.3 ± 0.3
3	trans 2-Butene (0.91)	3-Methyl-1-butene (0.70)	100	60	7.1 ± 0.7
4	1-Pentene (0.69)	2-Methyl-1-butene (0.72)	120	51	5.2 ± 0.2[b]

[a] The general procedure is given in the Experimental section: Temp., 0°C; TS-1, 3.9 g/liter; [H$_2$O$_2$], 0.15 M; solvent, methanol.

[b] TS-1, 4.9 g/liter.

TABLE 4

Additive Effect on the Rate of Epoxidation
of 1-Butene[a]

n	Additive (M)	H_2O_2 (conv. %)	Selectivity (% on H_2O_2)
1	—	96	96
2	LiCl (0.21)	91	84
3	$NaNO_3$ (0.18)	92	85
4	HF (0.007)	10	95
5	NH_4F (0.15)	12	b
6	[c]	30	92
7	CF_3COOH (0.19)	95	64[d]
8	CH_3COOLi (0.18)	~0[e]	—

[a] See Experimental section for reaction conditions. [1-butene], 0.90 M; [H_2O_2], 0.10 M; TS-1, 5.9 g/liter; Temp., +5°C; 1 h; solvent, methanol.

[b] Not determined.

[c] TS-1 (10 g) was refluxed beforehand with NH_4F in water (50 ml, 1.5 M) for 1 h, washed with water, dried, and calcined at 400°C. Reaction temperature −5°C.

[d] Solvolysis products 27%.

[e] Adding CF_3COOH (0.19 M) yielded analogous results to entry 7.

The epoxidation of *trans* 2-butene at 60°C was similarly carried out. *Trans* 2,3-epoxybutane and erythro 2-hydroxy-3-methoxybutane were the only products.

Epoxidation of cis 2-Butene in Water

Aqueous hydrogen peroxide (20 ml, 0.19 M), TS-1 (0.13 g), and *cis* 2-butene (1.0 g) were charged into a 35-ml-volume glass pressure vessel. The slurry was heated for 1.5 h at 25°C, under vigorous stirring. Then, acetone (as the solvent, 10 ml) and benzene (GLC internal standard, 0.067 g) were added. The conversion of hydrogen peroxide was 51%. *Cis* 2,3-epoxybutane (80% selectivity on H_2O_2) and 2,3-dihydroxybutane (6% selectivity on H_2O_2) were produced.

Epoxidation of 1-Butene. Additive Effects

The procedure for 1-butene was adopted. LiCl, HCl, $CH_3CO_2Li \cdot 1/3H_2O$, NaOH, HF, NH_4F were added at the beginning of the reaction. Results are illustrated in Table 4.

Epoxidation of Propylene in the Presence of Tetrapropyl Ammonium Hydroxide

A hydrogen peroxide solution in methanol (50 ml, 0.092 M), TS-1 (0.20 g), aqueous tetrapropylammonium hydroxide (1.5 g, 29.6 wt%), and propylene (3.7 g) were charged into the 300-ml glass pressure vessel. The slurry was stirred at 30°C for 10 min. Hydrogen peroxide conversion and selectivity to propylene oxide were 90 and 97%, respectively (*11*).

RESULTS

Titanium silicalite is an extremely effective catalyst for the epoxidation of unhindered alkenes, under mild conditions. The reaction of C_4–C_8 *n*-olefins, between −5 and 50°C, with dilute solutions of hydrogen peroxide in methanol, is fast and selective (Table 1). In the epoxidation of 1-butene at 0°C, hydrogen peroxide conversion and selectivity to 1,2-epoxybutane were 90 and 97%, respectively, after 1 h (Fig. 1). Glycols and glycol monomethylethers were the principal by-products. The oxidation of methanol to formaldehyde and the decomposition of hydrogen peroxide to oxygen, were both negligible under these conditions. To the limits of detection, by-products of homolytic reactions were not observed, even for [olefin] = [H_2O_2]. Side reactions were increasingly important and selectivities lower, as the branching of the alkene increased.

Electron-deficient olefins also could be epoxidised at near room temperature. High yields to epichlorohydrin and glycidol were produced by allyl chloride and allyl alcohol, respectively, at 45°C (Table 1). Styrene yielded 2-phenylacetaldehyde, 2-phenyl-2-methoxyethanol, and minor amounts of benzaldehyde at 60°C (*10b*). The dimethyl acetals of aldehydes were also detected. Under analogous conditions, styrene oxide, a likely precursor in the reaction, decomposed to a similar product composition.

The rate of reaction was much dependent on the nature of the olefin, i.e., the molecular weight, the presence of substituent
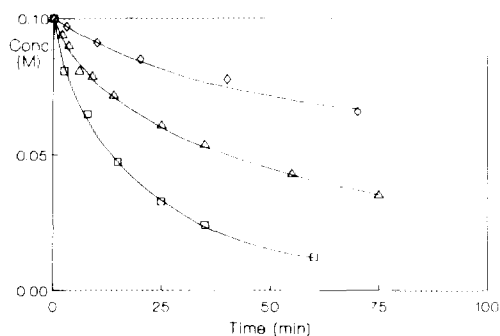
FIG. 1. Epoxidation of olefins in methanol. The concentration of hydrogen peroxide is plotted against time. Reaction conditions: Temp., 0°C; TS-1, 6.2 g/liter; H_2O_2 0.099 M; olefin, 0.90 M. (□) 1-butene, (△) 1-pentene, and (◇) allyl chloride.

groups, the number, the position and the electronic properties of the latter, and the steric configuration. Kinetics were slowed by increasing the chain length or the cross-section of the olefin, and by electron-withdrawing groups. Thus, the olefins exhibited the following order of reactivity: 1-butene > 1-pentene > 1-hexene > 1-octene ≫ cyclohexene, and 1-butene > allyl chloride > allyl alcohol (Fig. 1, Table 1). 1-Hexene was epoxidised two orders of magnitude faster than cyclohexene. The initial rate of reaction of electron-deficient allyl chloride and allyl alcohol was about 14 and 30 times slower than that of 1-butene, respectively.

The relationship between alkyl substituents and reactivity of the double bond was better shown by competition kinetics on C_4 and C_5 olefins (Tables 2 and 3). Scheme 1 shows the self-consistency of kinetic results, as illustrated by Table 2 (26). For any closed circuit in the Scheme, the product of selectivity coefficients S should be equal to unity. Thus, going from cis 2-butene to isobutene to trans 2-butene to 1-pentene to 1-butene, the product of S-values is 1/3.4 × 1/4.7 × 3.4 × 1.7 × 2.7 = 0.98, in good agreement with expected value of unity. For other sets of olefins, although the agreement might be lower, it is still satisfactory. By this method, the value of 1-butene/trans 2-

butene relative rate was estimated to be close to 6.

C_4 and C_5 olefins exhibited the following order of reactivity: trans 2-butene [1.0] < 1-pentene [3.4] < isobutene [4.7] < 1-butene [~6] < cis 2-butene [16.2], and trans 2-butene [1] > 2-methyl-2-butene [0.91] > 2-methyl-1-butene [0.23] > 3-methyl-1-butene [0.14]. This ordering disagrees with that which would be expected for peracids and other electrophilic epoxidizing agents (2, 3). It is immediately apparent that steric constraints due to alkyl substitution at the double bond play a major role in this trend. Thus, 1-butene and 1-pentene reacted faster than isobutene and 2-methyl-1-butene, respectively (Table 2, entry 3, and Table 3, entry 4), whereas trans 2-butene was epoxidized 1/16 as fast as the cis isomer (Table 2, entry 5).

In agreement with earlier studies (11), the solvent exerts a major effect on kinetics: $CH_3OH > C_2H_5OH > t\text{-}C_4H_9OH$ (Fig. 2). The yields decreased and the extent of side reactions grew steadily in the same order. In ethanol, selectivity to 1,2-epoxypentane was 71%, while the remainder of the hydrogen peroxide was consumed by the oxidation of the solvent. In t-butanol, t-butyl hydroperoxide was also produced and built up in the reaction mixture (27), but did not af-
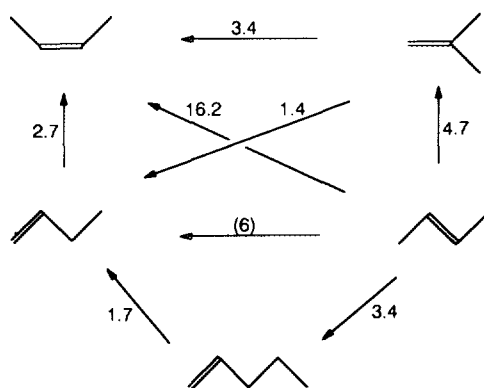
SCHEME 1. The figure at each arrow is the v_1/v_2 ratio. The head of each arrow points to the olefin pair for which $v_1 > v_2$.
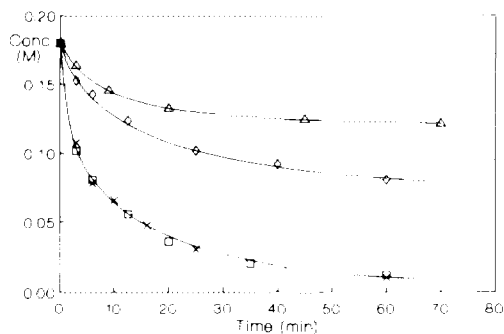
FIG. 2. Effect of the solvent on the epoxidation of 1-pentene. The concentration of hydrogen peroxide is plotted against time. Reaction conditions: Temp., 25.0°C; TS-1, 6.2 g/liter; H_2O_2, 0.18 M; 1-pentene, 0.9 M. ($\times$) methanol, ($\square$) methanol/TBHP, ($\diamond$) ethanol, and ($\triangle$) t-butanol.
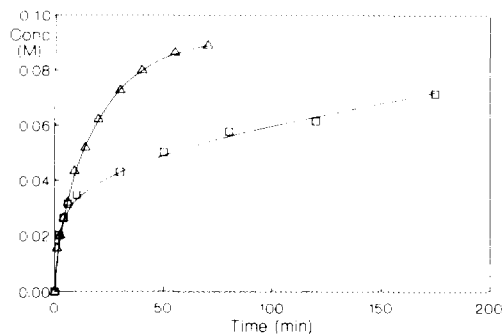

FIG. 4. Effect of TS-1 crystallite size on the epoxidation of 1-butene in methanol. The concentration of 1,2-epoxybutane is plotted against time. Hydrolysis products are not shown. Reaction conditions: Temp., -5°C; [Ti], 0.004 M; H_2O_2, 0.12 M; 1-butene, 0.9 M. ($\triangle$) 0.1–0.3 μm TS-1, and ($\square$) 2–3 μm TS-1.

fect the epoxidation reaction. In contrast with simple olefins (11), the epoxidation of allyl alcohol was unaffected by water, up to about 65% H_2O_2 conversion (Fig. 3).

Small amounts of alkali metal hydroxides or acetates improved the yields up to almost quantitative results. Under these conditions, rates were not significantly reduced. Further increasing the concentration of the base decreased and eventually inhibited
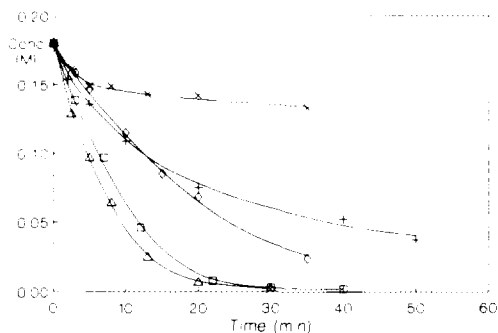

FIG. 3. Epoxidation of allyl chloride and allyl alcohol. The reactions of the former are carried out in methanol. The concentration of hydrogen peroxide is plotted against time. Reaction conditions: Temp., 45°C; TS-1, 6.2 g/liter; H_2O_2 0.18 M; olefin, 0.9 M. ($\square$) allyl chloride, ($\times$) allyl chloride in the presence of LiCl 0.2 M, ($\triangle$) allyl chloride in the presence of LiCl 0.2 M + HCl 0.1 M, ($\diamond$) allyl alcohol in methanol, and (+) allyl alcohol in water.

TS-1 activity (Table 4). It should be noted that strong bases of bulky cations, such as tetrapropylammonium hydroxide, which are unable to diffuse inside TS-1 channels, did not affect catalytic activity at any concentration. Metal salts of strong acids yielded different results. Lithium chloride and sodium nitrate did not slow the epoxidation of 1-butene at 0°C, while the former clearly inhibited the epoxidation of allyl chloride, at 45°C (Fig. 3). Hydrochloric acid improved rates. Fluorides, namely HF and NH_4F, were strong inhibitors even at low concentration (Table 4).

The epoxidation of cis and trans 2-butenes, carried out in methanol or aqueous solutions between -5 and 60°C, was completely stereoselective (10d). The stereochemistry of the double bond remained unchanged. Consistently, cis 2,3-epoxybutane and threo 2-hydroxy-3-methoxybutane were produced by the former, whereas trans 2,3-epoxybutane and erythro 2-hydroxy-3-methoxybutane were produced by the latter. We have previously shown that the solvolysis of the oxirane ring, catalysed by TS-1/H_2O_2, occurs with inversion of configuration (23).

According to Fig. 4, the rate of epoxidation was initially independent of the size of TS-1 crystallites, becoming slower with
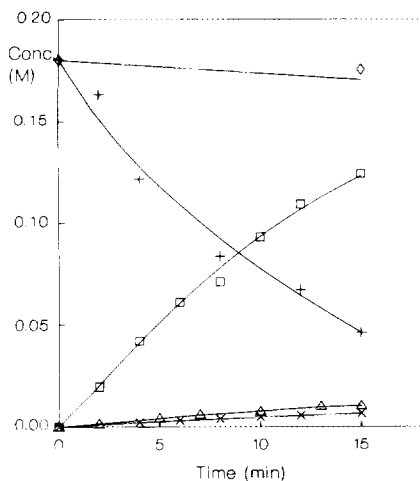
FIG. 5. Competitive oxidation of allyl chloride (0.9 M) and n-hexane (0.9 M) as compared to that of n-hexane (0.9 M). The concentration of hydrogen peroxide and products are plotted against time. Reaction conditions: Temp., 45°C; TS-1 6.2 g/liter: solvent, methanol. Competitive oxidation: (+) hydrogen peroxide, (□) epichlorohydrin, and (×) hexanols + hexanones. Oxidation of n-hexane: (◇) hydrogen peroxide and (△) hexanols + hexanones.

larger crystals only after 30% H_2O_2 conversion. At the same time, solvolysis products were detected in the reaction mixture of the latter.

Although useful to mechanistic studies, competition kinetics between olefins and paraffins could not be easily made, because of the much faster rate of reaction of the former. Nevertheless, we carried out such an attempt by selecting the most reactive paraffin (n-hexane) and one of the less reactive olefins (allyl chloride) (Fig. 5). Bearing in mind that the concentration of individual products was much too low for accurate GLC analyses (10^{-4} to $10^{-3} M$), the initial rate of oxidation of n-hexane in the presence of allyl chloride (7.5×10^{-4} M·liter^{-1}·min^{-1}) did not significantly differ from that in its absence (8.5×10^{-4} M·liter^{-1}·min^{-1}).

DISCUSSION

It is widely accepted that Group IV–VI metal catalysed epoxidations with hydrogen peroxide or with organic hydroperoxides and the epoxidations with peracids occur by a heterolytic mechanism in which the active oxidising species acts as an electrophile. The rate of reaction is enhanced or lowered by substituent groups, mostly on the basis of electron-donating or -withdrawing properties. Thus, inductive effects predominate over steric constraints. *Cis* and *trans* isomers are epoxidised at approximately the same rate, with retention of configuration. Yields to epoxides are high. By-products due to homolytic pathways are negligible (2, 3, 28, 29).

Similarly, titanium silicalite as an epoxidation catalyst is characterised by high selectivity, stereospecificity, and electrophilic behaviour. The latter is frequently masked by steric factors, imposed by the TS-1 pore system. Nevertheless, it is immediately apparent in the reactivity trend of similarly hindered olefins. Both sequences, allyl alcohol < allyl chloride < 1-butene (Fig. 1, Table 1) and 3-methyl-1-butene < 2-methyl-1-butene < 2-methyl-2-butene (Table 3), are in the order of increasing electron density at the double bond. Also, the ratio between the rates of *cis* 2-butene and 1-butene, although significantly lower than those reported for peracids and for homogeneous catalysts (22, 28), is consistent with an electrophilic epoxidising species.

What distinguishes titanium silicalite is shape selectivity, which results from active sites being situated in a channel system of about 0.55 nm average diameter. Thus, branched and cyclic olefins react more slowly than linear α-olefins, although the double bond in the former is a better nucleophile. Both restricted transition state shape selectivity and diffusivity effects of reagents and products contribute to this ordering, and their relative weight is not easily distinguished in most cases. However, consistently with the molecular size of the olefins, it is likely that the *cis/trans* relative rate relationship results from the former effect, while the second is the determining factor for $v_{1\text{-hexene}} \gg v_{\text{cyclohexene}}$. The reactivity trend

of linear α-olefins is consistent with the decrease of diffusivity in zeolites with increasing molecular weight, but contradicts that reported for the oxyfunctionalization of n-alkanes (24). With the latter, the rates of reaction went through a maximum shown by n-hexane, as the result of opposite inductive and diffusivity effects of the alkyl chain. Thus, the epoxidation appears to be a more sterically demanding reaction.

As to the mechanism, we have previously shown that, in at least one case, TS-1 operates by a homolytic pathway. A radical intermediate, formed by hydrogen peroxide and lattice Ti, is involved in the H-abstraction step of saturated C–H bonds (24). However, proposing that species as the active epoxidizing species as well would not account for the experimental facts. The high yields to epoxes, up to quantitative results in the most favourable cases (11), the absence of by-products normally observed in homolytic epoxidations (28, 29), and the stereospecificity of the reaction can only be interpreted in terms of the nonradical nature of the mechanism leading to epoxes. Furthermore, both solvent and shape selectivity effects differ significantly in the epoxidation of olefins, pointing to a different active species (24).

Species I has been regarded by others as the key intermediate in TS-1 catalysis (30, 31). Direct evidence for this species being formed at Ti sites have not been given, although it cannot be discharged on the basis of present knowledge (23). However, species I suffers from major shortcomings. These are: the inadequacy in explaining the effects of solvents, bases, and acids on kinetics, the unusually high catalytic activity of titanium silicalite with dilute solutions of hydrogen peroxide in protic media, and the chemical inertness of known titanium peroxides.
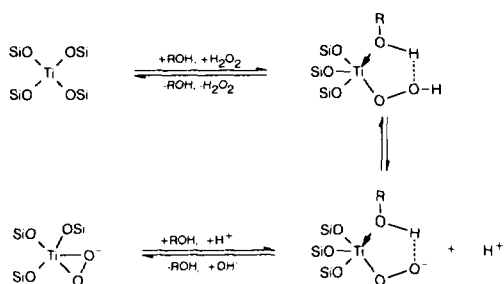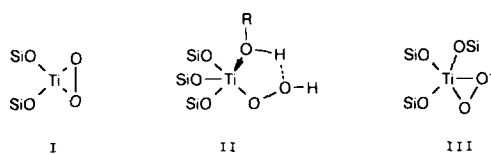
SCHEME 2

We have drawn attention to the chemical stability of the latter (24). Nevertheless, two cases recently reported by Ledon and Varescon (32) and by Trost and Bergman (33), respectively, concerning the deactivation of epoxidation catalysts by side-on coordination of peroxide ligand to the metal, deserve further mention. (TPP)Ti(O$_2$) and Cp*MoO(O$_2$)Cl peroxides (TPP = tetraphenylporphyrin, Cp* = pentamethylcyclopentadienyl), formed by side-reactions of corresponding oxo complexes with alkylhydroperoxides, were the poisoned form of the catalysts, (TPP)TiO and Cp*MoO$_2$Cl, respectively. Otherwise, metal–alkyl hydroperoxide complexes, M–OOR (M = Ti, Mo), were proposed as active species for the transfer of oxygen to the double bond.

Peroxide I fails to account for the close relationship between solvents and kinetics. The molecules which enter the internal sieve structure of TS-1 are held by physical forces of the Van der Waals type or, otherwise, by means of chemical bonds at lattice Ti (23). Since the average diameter of the channels is of the order of 0.55 nm, a value which is close to the critical diameter of the entering molecules, there is no space available for multilayer adsorption and therefore for reagent molecules experiencing solvent effects. The dependence of the rate of reaction on the solvent is better explained by assuming that the latter has a primary role in one of the elementary steps of the epoxidation mechanism. On this basis, a straightforward interpretation of the events is offered by species II.
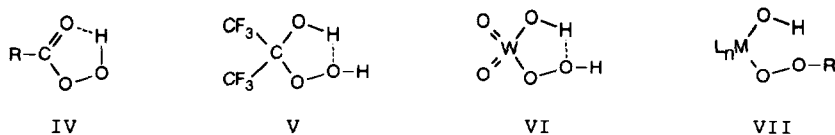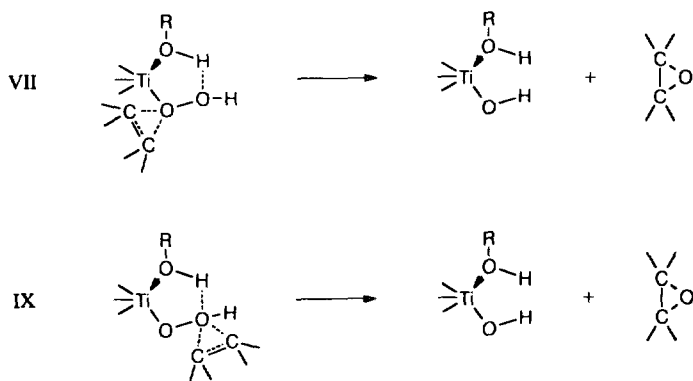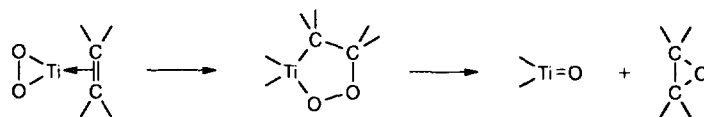
SCHEME 3

The latter is consistent with the distinguishing features of TS-1 catalysis, i.e., the acid properties of TS-1/H$_2$O$_2$/ROH, the effect of acids, bases and solvents on kinetics, and the lack of inhibition of protic compounds (*11, 23, 24*). The central role played by the protic molecule on the stability of II answers the question why titanium silicalite is such an active epoxidation catalyst in dilute protic solutions of hydrogen peroxide, a medium otherwise known to inhibit Group IV–VI metal oxide based catalysts (*28*). The reactivity trend in alcoholic media, methanol > ethanol > *t*-butanol, is likely to be the result of decreasing electrophilicity and increasing steric constraints of species II. As the size of ROH grows larger, both the formation of II and the approach of the olefin to it, in the oxygen-transfer step, are increasingly hindered. Accordingly, TS-1 shows highest and lowest catalytic activity in methanol and *t*-butanol, respectively. In aqueous solutions, the concentration of II

is likely to be decreased by the poorer donor properties of the water ligand, without being compensated by the increase of electrophilicity. This might explain retarding effects on kinetics shown by water, in the epoxidation of propylene (*11*).

The effects of crystal size, acids, and bases on the catalytic activity are most probably related to acid–base properties of species II (Scheme 2). The time course of 1-butene oxidation, with catalysts having different crystal size, suggests that the deactivation of large crystal TS-1 occurs earlier, due to the faster occlusion of the channel system by slow diffusing solvolysis products. We have previously shown that the presence of strong acid sites enhances the rate of deactivation of M–TS-1 (M = Al, Ga, Fe) (*12*). Small amounts of basic compounds improve the selectivity by decreasing the acid strength inside the pore system of TS-1. At higher pH, however, stable peroxides III are formed at Ti sites (Scheme 2)

SCHEME 4

SCHEME 5

(34). These are inert to reactions with olefins, since the presence of a negative charge greatly reduces their electrophilic properties. Strong acids shift the equilibrium toward undissociated species II, reestablishing the catalytic activity of titanium silicalite.

The close similarity in the results shown by both HF and NH_4F indicates that the inhibition by fluorides might result from a different origin. Competition of F^- ions with H_2O_2 for coordination at Ti sites, is the likely interpretation *(24)*.

Peracid-like structure II closely resembles IV–VII (see Scheme 3), which are the active epoxidizing species proposed for RCO_3H *(35, 36)*, α-substituted hydroperoxides *(37)* such as CF_3COCF_3/H_2O_2 *(3, 18)*, WO_3/H_2O_2 *(14–16)*, and $ML_n/ROOH$ (where M = Ti, V, Mo, W, and R = Alkyl, Aryl) *(19, 20)*, respectively. The O–O bond is polarised by an electron-withdrawing group, which in TS-1 is the strongly acidic Lewis centre $[-Ti(OSiO_3)_3]$. In species II, as in other cases, heterolytic cleavage is further assisted by hydrogen bonding through a five-membered interaction. These arguments strongly support that the oxygen-transfer, from the inorganic peracid II to the double bond, occurs by a similar mechanism to that generally accepted for species IV–VII. Following earlier proposals for peracids *(35, 36)*, later extended by Sheldon *(19)*, and by Chong and Sharpless *(20)* to include Group IV–VI transition metal catalysts, two mechanisms can be envisaged (Scheme 4).

These are in contrast with a recent proposal put forward by Huybrechts *et al.* *(38)*. In their view, the oxygen-transfer to the double bond occurs via the intramolecular reaction of an olefin–titanium–peroxo complex, formed by prior coordination of both the olefin and H_2O_2 at Ti sites (Scheme 5). The inhibition shown by 1-octene, in the competitive oxidation of *n*-hexane in a water/acetone mixture, was taken to support this mechanism. However, we were unable to detect any such inhibition under our reaction conditions. The oxidation of *n*-hexane, in a homogeneous methanol solution, was not significantly affected by the presence of allyl chloride, whereas competition experiments with other olefins were not feasible.[2]

The reactivity trend of lower olefins is more consistent with IX than with VIII (Scheme 4). In both mechanisms, steric constraints in the transition state result from repulsive interactions of alkyl substituents on the olefin with either coordinated ROH and framework Si and O atoms. The extent of such interactions is higher for two methyl groups in the *trans* position, as shown by

[2] The results of Huybrechts *et al.* *(38)* might be explained as well by the impurities present in the catalyst. Figure 5 of Ref. *(38)* clearly shows that TS-1 samples used in the work were admixtures with TiO_2, which is otherwise known to decompose homolytically hydrogen peroxide and start radical chains (as to the UV–vis spectra of TS-1 and TiO_2, see also Ref. *(39)*). Furthermore, the reaction mixture was made up of two liquid phases, in one of which acetone was the main component. Hydrogen peroxide will preferentially dissolve in the latter, to afford nonnegligible amounts of organic peroxides *(40)*, which, at the high temperature used in the experiment and in the presence of Ti compounds, will also take part in homolytic reactions. Thus, the oxidation of *n*-hexane might have been in part the result of radical chains that were inhibited by excess olefin in the competitive experiment *(19, 28)*. We wish also to stress that it is most unlikely that Ti^{IV} (and any other high-valent Group IV–VI transition metal) would preferentially coordinate an olefin ligand, in the presence of oxygenated molecules (water, alcohols, ketones, and the like).

the relative rate of reaction of *cis* and *trans* 2-butenes. This is very reminiscent of the epoxidation of *cis* and *trans* 2-octenes, catalysed by a manganese (III) porphyrin complex *(41)*. In the latter the active site is centered in a planar macromolecule, which simulates the steric effects of a solid catalyst surface.

Mechanism VIII is disfavoured on the basis of steric arguments. According to Chong and Sharpless, the optimum direction of approach of the olefin to the oxygen is from the back side and along the O–O bond axis *(20)*. Making the same assumption for VIII, alkyl groups on the olefin would be forced into close proximity with framework siloxane bonds, giving rise to serious steric hindrance. On the other hand, in mechanism IX the olefin approaches distal oxygen,[3] which molecular models show to protrude at roughly the centre of the zeolitic channel, minimising in this way the interactions with the surface, while keeping low those with coordinated methanol. In our view, mechanism IX, which is more similar to earlier proposals for peracids than to more recent ones for transition metal catalysts, is more attractive than VIII in representing the epoxidation reaction.

As to the relationship between this mechanism and that of paraffin oxidation, while in the former the species II is directly involved in the oxygen-transfer step, in the latter it is only a precursor of the yet unknown intermediate which homolytically abstracts an H-bond from the alkane *(24)*.

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