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Oxidation of Alcohols with H_2O_2 Catalyzed by Titanium Silicalite-1

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Primary and secondary alcohols are oxidised by H_2O_2 in the presence of titanium silicalite-1 to carbonylic compounds. Reaction rates follow the general trend secondary > primary > methanol. Rates are sensitive to position effects of the OH group, to chain branching effects, and to molecular size of the alcohol. Kinetic orders with respect to H_2O_2 are generally close to zero, while those with respect to the alcohol are strongly affected by the solvent used. The kinetic pattern is interpreted in terms of an interaction of the lattice titanium atom of titanium silicalite-1 with H_2O_2. The kinetic order with respect to the alcohol can be interpreted either in terms of titanium–alcohol adducts or with a selective alcohol sorption in the catalyst pores. The reaction pattern is consistent with a process taking place essentially inside the zeolite channels, with a transition-state-restricted shape-selectivity. The nature of the titanium hydroperoxide involved in the intermediate complex is discussed. © 1994 Academic Press, Inc.

INTRODUCTION

Selective alcohol oxidation to form aldehydes and ketones by means of a low cost oxidant and a simple, stable catalyst is a subject of current interest in catalysis (1), because of important industrial implications inherent to this problem. Hydrogen peroxide is a suitable oxidant, and moreover the environmental damage is reduced. As to the catalyst, a variety of metal complexes have been investigated, particularly molybdenum (2, 3), tungsten (2, 4), copper (5), and ruthenium (6, 7) complexes. Catalysis is generally carried out in homogeneous solution; the use of phase-transfer conditions has also been reported (2).

We reported recently (8) a general outline of the catalytic activity exhibited by titanium silicalite (TS-1) in the oxidation of various molecules (substrates) with H_2O_2. Preliminary data on the oxidation of alcohols were given in this review. Furthermore, two of them (methanol, tertiary butanol) play an important role as suitable solvents for TS-1 catalyzed reactions in general, and have been particularly used for epoxidation (9–11), aromatic hydroxylation (12, 13), hydrocarbon oxidation (14–16), and ketone ammoximation (17). Here we give more information on the alcohol oxidation and the role alcohols play as solvents with the H_2O_2/TS-1 system.

EXPERIMENTAL

All reagents were commercial grade, and were used without further purification. Hydrogen peroxide 60% w/w (d = 1.26) was purchased from Interox.

The preparation of TS-1 has been described in earlier literature (18–20); more details have been recently given (11). Elemental analyses gave TiO_2 2.6%, SiO_2/TiO_2 molar ratio = 51. IR and XRD spectra of the product were in agreement with literature data (11).

Experimental Procedure

In a typical kinetic experiment, TS-1 was stirred in the solvent using a mechanical stirrer and a thermostated bath. Amounts for each experiment are given in the figure legends. The solvent (if any), substrate(s), co-reagents if any (H_2O, HCl, aldehyde, ketone) and catalyst were added in this order under stirring. After temperature equilibration, 60% H_2O_2 was added from a precision syringe (the addition time was 5–30 s, depending on the volume to be added). Samples were withdrawn by a pipette for analyses.

Analytical Procedures

In general, reactions carried out with excess H_2O_2 and competition reactions were followed by determining the formation of carbonylic product(s) by glc. Response factors were determined using solutions of authentic samples. Gas chromatographic analyses were performed using a Perkin–Elmer Sigma 3B chromatograph, and packed columns containing the following stationary phases: 0.1% SP1000 on Carbopack (2-butanol, 2-pentanol, 3-pentanol in MeOH); 10% Carbowax 400 on Chromosorb W (2-butanol in TBA and in H_2O); 10% SE 52 added with 2% Carbowax 400 on Chromosorb W (competition of 2-pentanol and 3-pentanol). A 50-m fused silica capillary column, 0.25 mm i.d., coating CP-SIL-5CB (WCOT, Chrompack) was used for 2-propanol in methanol solution.

Reactions carried out in the presence of excess substrate were followed by H_2O_2 titration (iodometric). In

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these cases, selectivities were always determined by both glc and gas volumetric determination of oxygen.

KINETIC RESULTS

Neat Alcohol Oxidation

Methanol, primary and secondary alcohols are oxidised to carbonylic compounds (8). Preliminary data were obtained in neat alcohols. Only carbonylic products (aldehyde, acetal, ketone) were detected in the reactions of CH_3OH or secondary alcohols. In the case of primary alcohols, products due to further oxidation (carboxylic acid and minor amounts of ester) were also found, depending on conversion. The H_2O_2 decomposition to O_2 is negligible in most cases. Reactivities and H_2O_2 decomposition to O_2 for several alcohols are compared in Table 1.

Tertiary alcohols react very slowly, producing alkyl hydroperoxides with an excellent alcohol selectivity. An important H_2O_2 decomposition was observed.

Kinetic experiments were carried out in different alcohols, using different concentrations of catalyst or H_2O_2.

For the reaction of methanol with H_2O_2, Fig. 1 shows the dependence of the reaction rate on the catalyst amount (expressed as weight %). Rates are proportional to the catalyst amounts, in the sense that the reaction times needed to achieve a given conversion are inversely proportional to the catalyst amounts. This behaviour is general for all alcohols tested.

The dependence of the reaction rate on the initial H_2O_2 concentration is shown in a plot of H_2O_2 conversions vs time (Fig. 2), relative to 1-propanol. The behaviour displayed is typical of a kinetic order <1. Also this type of behaviour is common to all other alcohols tested.

TABLE 1

Oxidation of Alcohols with TS-1/H_2O_2[a] Time of Half H_2O_2 Conversion and Extent of H_2O_2 Decomposition

Alcohol	$t_{1/2}$[b] (h)	H_2O_2 decomposition[c] (%)
Methanol	8.5	13
Ethanol	0.7	2.5
1-Propanol	1.0	5
1-Butanol	1.3	6
1-Octanol	3.0	—
2-Methyl,1-propanol	3.4	—
2-Propanol	0.01	<0.5
2-Butanol	0.05	<0.5
2-Pentanol	0.06	<0.5
3-Pentanol	0.9	5
Cyclohexanol	35	50

[a] Solvent, neat alcohol; $T = 45°C$; Catalyst = 5 wt%; $H_2O_2 = 0.50$ mol/liter.

[b] 50% H_2O_2 conversion times.

[c] % H_2O_2 decomposition to O_2 for complete conversion.

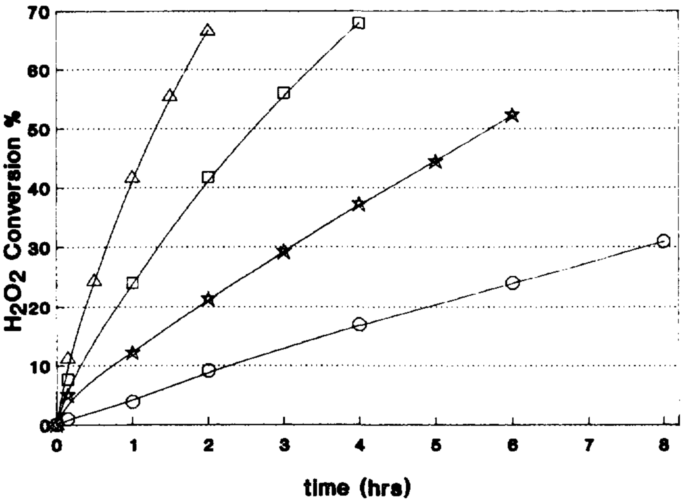


FIG. 1. Oxidation of neat CH_3OH with H_2O_2/TS-1: catalyst concentration effect. $T = 45°C$, $H_2O_2 = 0.57$ mol/liter; ○, 2.5 wt%; ☆, 5 wt%; □, 10 wt%; △, 20 wt%.

No inhibition effect was shown by the initial addition of reaction products (0.5 M propionic aldehyde, 1 M H_2O). Hydrochloric acid somewhat increases the kinetics (15% faster with 0.05 M HCl), similar to other TS-1 catalyzed reactions (14).

Oxidation of Alcohols in Methanol as Solvent

The oxidation of secondary alcohols can be studied in methanol, since their oxidation rates are normally much higher than that of methanol itself. Both the reactivity

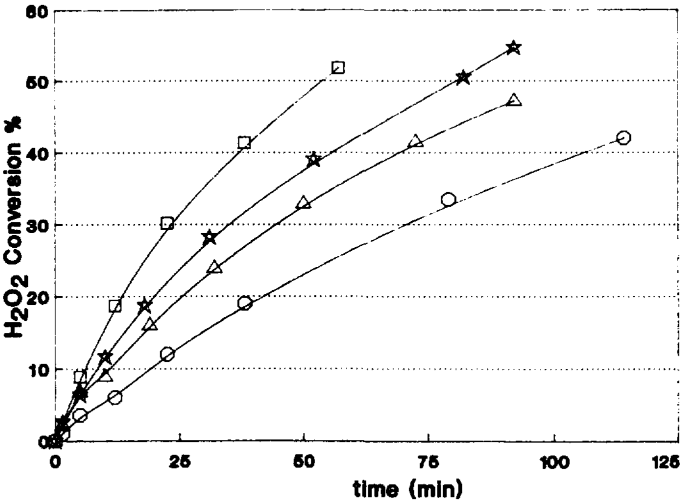


FIG. 2. Oxidation of neat 1-propanol with H_2O_2/TS-1: H_2O_2 concentration effect. $T = 45°C$, Cat = 4 wt%. □, 0.305 mol/liter; ☆, 0.566 mol/liter; △, 0.912 mol/liter; ○, 1.408 mol/liter.

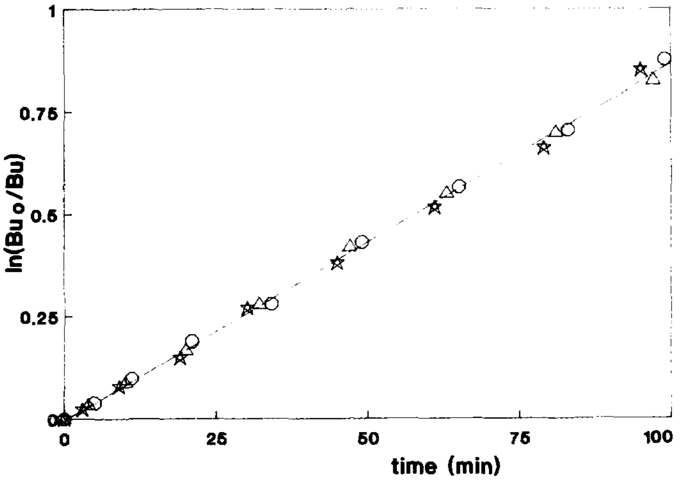


FIG. 3. Oxidation of 2-butanol with H_2O_2/TS-1 in methanol solution: 2-butanol concentration effect. H_2O_2 = 0.70 mol/liter, T = 45°C, Cat = 4 wt%. △, 0.087 mol/liter; ☆, 0.173 mol/liter; ○, 0.260 mol/liter.

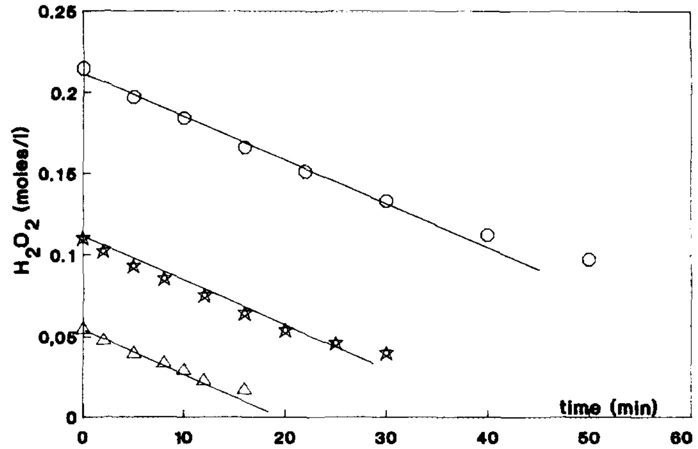


FIG. 4. Oxidation of 2-butanol with H_2O_2/TS-1 in methanol solution: H_2O_2 concentration effect. 2-butanol = 0.55 mol/liter, T = 45°C, Cat = 2.5 wt%. △, 0.055 mol/liter; ☆, 0.11 mol/liter; ○, 0.215 mol/liter.

trend and selectivities are similar to those observed for neat alcohols.

The substrate studied in most detail was 2-butanol. Solvent oxidation and H_2O_2 decomposition are negligible.

Kinetic runs carried out in the presence of different catalyst concentrations show that rates are proportional to the catalyst amounts, similarly to Fig. 1.

The substrate concentration effect was studied using a H_2O_2 excess. Kinetic runs carried out with different initial 2-butanol concentrations fit a first-order plot with coincident lines (Fig. 3). The H_2O_2 concentration effect was studied using an excess 2-butanol. Kinetic runs carried out with different initial H_2O_2 concentrations fit satisfactorily a zero order plot (Fig. 4), except at high conversions, when the H_2O_2 concentrations are low.

Similar results were obtained with 2-propanol, 2-pentanol, or 3-pentanol in methanol. First order constants for the four secondary alcohols, as obtained from kinetics in H_2O_2 excess (plots of the type in Fig. 3), are reported in Table 2. No inhibition effect due to the product addition was detected.

Competition kinetics were carried out with pairs of secondary alcohols as substrates in methanol solutions. An example is reported in Fig. 5; rate ratios, as calculated from product concentration ratios, are in good accord with reactivities indicated in Table 2.

Oxidation of Alcohols in Solvents Other Than Methanol

Solvents to be chosen should be sufficiently inert to avoid complicating side reactions. Suitable reaction media are H_2O or tertiary butanol (TBA).

Kinetic runs for the oxidation of 2-butanol in TBA show a striking difference with respect to the behaviour in methanol: kinetics of H_2O_2 conversion in the presence of a substrate excess fit neither first- nor zero-order plots. The intermediate situation is illustrated in a plot of H_2O_2 conversion vs time (Fig. 6).

On the other hand, the kinetics of susbtrate oxidation in the presence of excess H_2O_2 are quite close to zero order, with parallel lines for different initial substrate concentrations (Fig. 7), except at high conversions, when the substrate concentrations are low.

Analogous kinetic tests were carried out in H_2O as the solvent giving an identical pattern as in TBA, with slightly higher k_{obs} values.

Zero order constants in TBA or H_2O as the solvent, as obtained from kinetics with H_2O_2 excess (as in Fig. 7), are reported in Table 2.

TABLE 2

Rate Constants for the Oxidation of Secondary Alcohols in Different Solvents[a]

Alcohol	k_{obs} in MeOH[b] (s^{-1})	k_{obs} in TBA[c] (mol $liter^{-1}$ s^{-1})	k_{obs} in H_2O[c] (mol $liter^{-1}$ s^{-1})
2-Propanol	0.49×10^{-4}	—	—
2-Butanol	1.25×10^{-4}	2.0×10^{-4}	2.9×10^{-4}
2-Pentanol	1.25×10^{-4}	4.0×10^{-4}	3.0×10^{-4}
3-Pentanol	1.5×10^{-5}	4.2×10^{-5}	3.5×10^{-5}

[a] Catalyst = 4.3 wt%; H_2O_2 = 0.70 mol/liter.

[b] T = 45°C. First-order constants, calculated from plots of the type in Fig. 3, in excess H_2O_2.

[c] T = 30°C. Zero-order constants, calculated from plots of the type in Fig. 7, in excess H_2O_2.

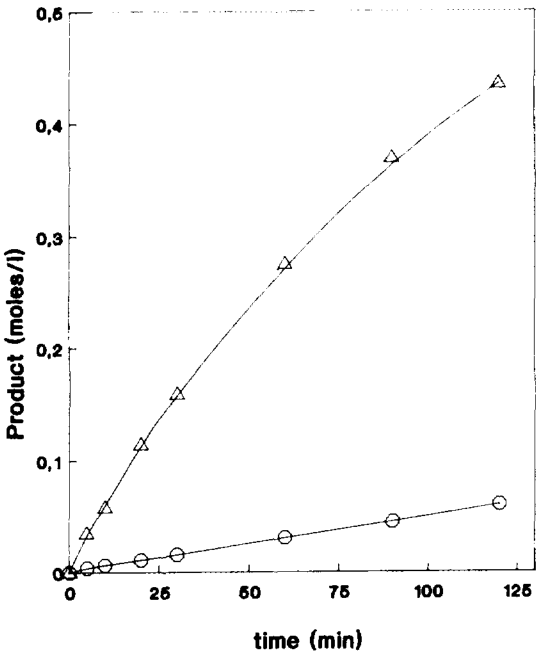


FIG. 5. Competition kinetics in methanol: 2-pentanol and 3-pentanol. 2-pentanol = 3-pentanol = 0.64 mol/liter, H_2O_2 = 0.61 mol/liter, T = 45°C, Cat = 4 wt%. △, 2-pentanone; ○, 3-pentanone.

DISCUSSION

Interpretation of the Kinetic Data

A summary of kinetic orders in different solvents is reported in Table 3.

An interpretation of this picture should take into account all possible interactions of the reactants and the solvent with the catalytic sites containing titanium. The following reaction scheme is in accord with the orders reported in Table 3:

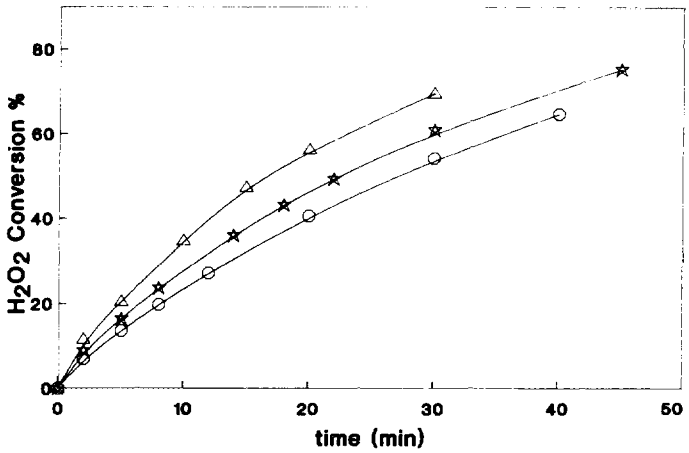


FIG. 6. Oxidation of 2-butanol with H_2O_2/TS-1 in TBA solution: H_2O_2 concentration effect. 2-butanol = 0.54 mol/liter, T = 30C, Cat = 3 wt%. △, 0.055 mol/liter; ☆, 0.11 mol/liter; ○, 0.22 mol/liter.

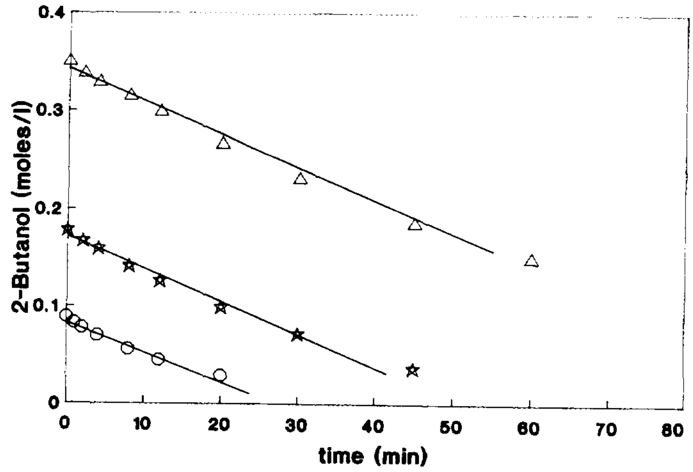


FIG. 7. Oxidation of 2-butanol with H_2O_2/TS-1 in TBA solution: 2-butanol concentration effect. H_2O_2 = 0.70 mol/liter; T = 30°C; Cat = 2 wt%. △, 0.089 mol/liter; ☆, 0.178 mol/liter; ○, 0.35 mol/liter.

$$[\text{Cat}] + \text{Solv} \overset{K_1}{\rightleftharpoons} [\text{Cat,Solv}] \qquad (\text{fast}) \qquad [1]$$

$$[\text{Cat}] + \text{ROH} \overset{K_2}{\rightleftharpoons} [\text{Cat,ROH}] \qquad (\text{fast}) \qquad [2]$$

$$[\text{Cat,Solv}] + H_2O_2 \overset{K_3}{\rightleftharpoons} [\text{Cat,Solv},H_2O_2] \qquad (\text{fast}) \qquad [3]$$

$$[\text{Cat,ROH}] + H_2O_2 \overset{K_4}{\rightleftharpoons} [\text{Cat,ROH},H_2O_2] \qquad (\text{fast}) \qquad [4]$$

$$[\text{Cat,ROH},H_2O_2] \xrightarrow{k} [\text{Cat}] + \text{Products} \qquad (\text{slow}). \qquad [5]$$

Here the symbols [Cat] represent the "free" catalytic sites, while the other species in brackets represent the adsorbed solvent or substrate, and the interaction products with H_2O_2.

The proposed scheme can account for the fact that the reaction rates in different solvents are similar (Table 2). Therefore, it is likely that the solvent does not take part in the slow step.

TABLE 3

Kinetic Orders Found for the Alcohol Oxidation[a] in Different Solvents

	Order with respect to		
Solvent	H_2O_2	Substrate	Example
Neat	0–1	—	Methanol
Neat	0–1	—	1-Propanol
Methanol	0	1	2-Butanol
H_2O	0–1	0	2-Butanol
TBA	0–1	0	2-Butanol

[a] Rates are proportional to catalyst amounts in all cases.

First, in the scheme above, the solvent and ROH are in competition for adsorption on the catalytic surface, where the catalytic sites are located. Then H_2O_2 will interact with either of the two adsorbed species, probably by coordination on titanium, as suggested by previous papers (21–23). The interaction of two distinct catalytic sites is unlikely, because titanium atoms are separated by a number of O–Si–O units in TS-1.

If Eqs. [1]–[4] represent fast equilibria, which is reasonable with respect to the reaction rates observed, the application of Langmuir–Hinshelwood isotherms gives

$$\text{rate} = k\,[\text{Cat},\text{ROH},H_2O_2] = \frac{kK_2K_4\,\text{ROH}\,H_2O_2\,C_{\text{tot}}}{1 + K_1 + K_2\text{ROH} + K_2K_4\text{ROH}\,H_2O_2 + K_1K_3H_2O_2} \qquad [6]$$

(C_{tot} is the total concentration of catalytic sites).

Kinetics in methanol. The rate law above corresponds to the behaviour in methanol, if the following assumptions are made:

$$K_1 \gg K_2 \gg 1, \quad K_3 \gg 1, \quad K_4 < K_3.$$

The meaning of these assumptions is that the adsorption of methanol on [Cat] is much stronger than that of substrate alcohols, which could be due simply to a mass effect (the solvent concentration is included in the term K_1), and that the coordination of H_2O_2 is stronger in the presence of adsorbed methanol than in the presence of other alcohols, which would be reasonable for steric reasons.

Using the assumptions above, the rate law can be simplified into

$$\text{rate} = \frac{kK_2K_4\,\text{ROH}\,C_{\text{tot}}}{K_1K_3} \qquad [7]$$

in accord with the orders found in methanol. The first-order constants reported in Table 2 (first column) have the meaning of a kinetic constant multiplied by an equilibrium factor, that in turn depends either on selective sorption and on the H_2O_2 coordination.

Kinetics in other solvents. The rate law (Eq. [6]) corresponds to the behaviour in TBA or H_2O with the assumptions

$$K_2 \gg 1 \gg K_1, \quad K_3 \sim K_4.$$

The meaning of these assumptions is that the adsorption of TBA or H_2O on [Cat] is much weaker than that of other alcohols, in spite of the mass effect. For TBA, this effect can be attributed to its cross-section, which is larger than that of linear C_4 or C_5 alcohols and is similar to the diameter of the zeolite channels. As to H_2O, it is known to have a very low sorption capacity on pure silicalite-1 in the vapour phase (24), particularly in comparison with alcohols (25), due to the absence of Al atoms in the framework, and it is reasonable to assume that the introduction of titanium into the silicalite framework does not change much this situation.

Using the assumptions above, Eq. [6] can be simplified into

$$\text{rate} = \frac{kK_4\,H_2O_2\,C_{\text{tot}}}{1 + K_4\,H_2O_2} \qquad [8]$$

in accord with the orders found. The zero-order constants in Table 2 (second and third columns), calculated at high H_2O_2 concentrations, should correspond to the kinetic constants k relative to the oxidative step in Eq. [5].

Neat alcohols. In neat alcohols, where $K_1 = K_2\,\text{ROH}$, and $K_3 = K_4$, the rate law yields ($K_1 = K_2 \gg 1$)

$$\text{rate} = \frac{kK_3\,H_2O_2\,C_{\text{tot}}}{1 + K_3\,H_2O_2}. \qquad [9]$$

In this treatment, the parameters considered are the surface adsorption, and the coordination of H_2O_2 by titanium on the catalytic sites. It was assumed that the diffusion rates do not affect the kinetics, which could turn out to be not completely true, if the actual diffusivities were measured. However, diffusivity measurements were beyond the scope of this work.

Mechanism

Since little is known of some of the reactivity factors, e.g., sorptions and diffusivities, and trends can only be supposed, it is advisable to limit comparisons to strictly homogeneous series.

The most general effect is the reactivity trend: $CH_3OH \ll$ primary $<$ secondary (Table 1). Beside this general trend, which is the same as that reported in most cases cited in the literature, some other effects can be inferred from the comparison of reactivities of different alcohols within homogeneous series, as specified in the following:

(i) The position of the OH group in the alkyl chain has an important effect on the oxidation rate, (compare 2-pentanol vs 3-pentanol. This is consistent with a process occurring inside the zeolite channels, with a restricted transition state selectivity effect. This discriminating effect is independent of the solvent: it is present in neat alcohols (Table 1), in methanol solution (first-order constants Table 2), and in H_2O or TBA (zero-order constants Table 2).

(ii) Branched alkyl chains give slower rates than linear ones (compare 2-methyl,1-propanol vs 1-butanol, Table

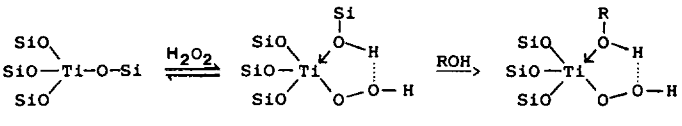
1). This type of effect could be related either to the steric requirement in the transition state or, more likely, to a low diffusion rate due to the presence of bulky groups. Similarly, the large cross section is likely to be responsible for the very low oxidation rate of cyclohexanol, particularly if compared with other catalytic systems (2).

(iii) The chain length has a minor effect on reactivity. This is probably due to the combination of opposite effects. Thus, 2-propanol is slightly slower than other 2-alkanols in methanol solution (Table 2), following the trend predicted for an electrophilic attack. Also, the same trend is found for the adsorption capacities of alcohols on silicalite-1 in the vapour phase (25). On the other hand, in neat alcohols an increase of the chain length produces a different trend (Table 1).

(iv) The low kinetic order respect to H_2O_2 ($0 < n < 1$), observed in all solvent systems, particularly in methanol ($n = 0$), can reasonably be interpreted in terms of an association of the titanium with a molecule of oxidant in an intermediate complex.

(v) The kinetic order respect to the substrate (1 in methanol, 0 in TBA, H_2O) gives no unambiguous answer to mechanistic questions. Generally speaking, this effect can be assigned to a catalyst–alcohol interaction. First, this interaction should account for the physical adsorption on the surface; however, the successive formation of a titanium complex with alcohol (either solvent or substrate) cannot be ruled out.

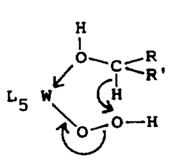
Speculating about the nature of the H_2O_2 adduct, Bellussi *et al.* (22) have brought evidence in favour of a cyclic adduct of type (II) shown below, coordinating both H_2O_2 and CH_3OH, for the interpretation of solvent effects in olefin epoxidations and in epoxide hydrolysis in methanol solution. If this assumption is correct, then it is likely that analogous structures can also be formed in the presence of alcohols other than methanol, provided the molecular size is not too large:



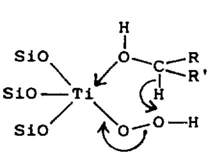
(I) (II)

Structures of type (I) or (II) should display an electrophilic character due to the partial positive charge on the distal oxygen, emphasised by hydrogen bonding. However, the alcohol oxidation should start with the C–H activation, and the intermediate actually responsible for this step could be better described by a structure that helps to elucidate how this bond is weakened.

In the case of alcohol oxidation in homogeneous catalysis with W complexes, intermediates of type (III) have been suggested by Jacobson *et al.* (26). The heterolytic cleavage of C–H gives rise to nucleophilic attack on the distal oxygen. Analogously, a situation of type (IV) can be suggested for TS-1. Possibly, an alcohol substrate could be coordinated in a structure (II) first, and shifted to (IV) before reaction:



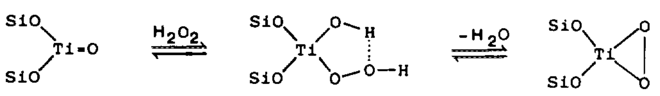
(III)



(IV)

The positional selectivity observed with secondary alcohols (Table 2) is in accord with this view: the strain of coordination bond angles in the transition state, as a result of the simultaneous C–H and O–O distance lengthening (and H–O shortening), would probably be affected by the length and size of the *R*,*R'* groups, and hence by the position of the OH. It is probably more difficult to account for the shape-selective effect with an alternative mechanism with an external nucleophilic attack from a noncoordinated alcohol molecule.

Besides the two-electron hypothesis above, also a one-electron process could be in accord with the experimental data. A possible source of radicals could be (III)Ti-OO˙, a resonance form of the peroxo species (VII). This could be formed from a titanyl (V), even though the presence of Ti=O groups in TS-1 has not been confirmed up to now by spectral investigations (21, 27). However, the hydroperoxide (VI) can be generated from a tetrahedral titanium as well (22):



(V) (VI) (VII)

Nevertheless, even if a homolytic mechanism is operating, the oxidation cannot probably be considered as a pure outer-sphere redox process. It is difficult to realize how a pure outer-sphere electron transfer could give the kind of selectivity reported in Table 2. Thus, the peroxide above (III)Ti-OO˙ could be a precursor of a reactive inner-sphere complex with the substrate. However, we have no indications at this stage for a more detailed design of a radical mechanism.

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