The solvent effect in the sulfoxidation of thioethers by hydrogen peroxide using Ti-containing zeolites as catalysts

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Abstract

The oxidation reaction of ethyl sulfide by hydrogen peroxide is investigated in various organic solvents, without catalyst and over Ti-containing zeolites (TS-1 and Ti-beta, respectively) as catalysts. It is shown that the reaction rate greatly depends on the nature of the solvent (protic or aprotic) whether the reaction is catalyzed or not. In the case of the catalyzed reaction, Ti-beta is more active and selective than TS-1 for all the solvents.

Keywords: Ethylsulfide; Ethylsulfoxide; Oxidation; Hydrogen peroxide; Titanosilicalites

1. Introduction

The interest of sulfoxides and sulfones in fine organic synthesis is well known, due to their increasing use as agrochemicals, pharmaceutical products, lubricants, etc. Sulfoxides are formed by partial oxidation of sulfides, which, upon further oxidation, are converted to sulfones,

$$R_1-S-R_2 \xrightarrow[(a)]{H_2O_2} R_1-SO-R_2 \xrightarrow[(b)]{H_2O_2} R_1-SO_2-R_2 \qquad (1)$$
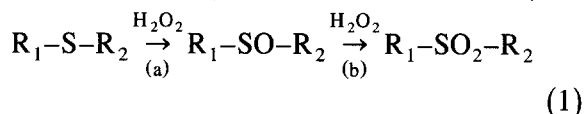
Hydrogen peroxide, H_2O_2, either alone or associated with various solvents or catalysts, is the most widely agent used for oxidizing or-

ganic sulfides [1]. H_2O_2 has taken new importance in recent years, because of its environmental implication, water being the only chemical by-product of oxidation reactions; moreover, it is less expensive and more accessible than the other oxidizing agents, such as peracids or hydroperoxides.

The use of transition-metal (Ti, Mo, Fe, V, W, Re, Ru) complexes as active catalysts for the selective oxidation of thioethers by H_2O_2 in homogeneous conditions has been reported by various authors [2–11]. It has been shown more recently that some of these metals (Ti, V), incorporated in a zeolitic framework are able to catalyse such an oxidation reaction [12,13]. The application of such transition metal-containing zeolites in the oxidation of various organic substrates, i.e. alkanes, alkenes, phenols, amines, sulfides [12,14–16], constitutes a significant

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breakthrough in the field of heterogeneous catalysis. The structure of the zeolite (MFI, BEA, MEL) plays an important role in the oxidation processes [17–20], but the nature of the solvent can also affect the reaction [21,22].

Nevertheless, systematic studies on the effect of the solvent in the oxidation reactions of organic substrates by H_2O_2 using Ti- (or V-) containing zeolites as catalysts are not reported. The purpose of the present study is to explore the influence of various solvents in the sulfoxidation of thioethers by hydrogen peroxide using Ti-beta and TS-1 as catalysts.

2. Experimental

2.1. Materials

Ethyl sulfide (98%) from Aldrich was used as supplied. Hydrogen peroxide (aqueous solution 31 wt%) was obtained from Prolabo. Methanol, analytical grade (SDS), ethanol, analytical grade (SDS), tert-butanol, HPLC grade (Sigma–Aldrich), acetonitrile, 99% (Aldrich), acetone, HPLC grade (Aldrich) and tetrahydrofuran, analytical grade (SDS) were used as solvents.

2.2. Catalysts

TS-1 and Ti-beta, with structure MFI and BEA, respectively, have been used as catalysts. The composition of the catalysts was $Ti/(Ti + Si) = 0.011$ and 0.008 for TS-1 and Ti-beta, respectively. Crystal size as determined by scanning electron microscopy (Cambridge Stereocan 260) was 0.1 μm for TS-1 isometric crystals and 0.4 μm for zeolite beta spheroidal grains. The presence of an absorption band corresponding at 48 000 cm^{-1} in DR-UV–vis spectra [13] indicates that Ti (IV) is incorporated in the framework of molecule sieves. No band corresponding to segregated TiO_2 particles was found to be present in this spectra.

2.3. Catalytic experiments

The catalytic sulfoxidation of ethyl sulfide with hydrogen peroxide was carried out in a glass flask equipped with a magnetic stirrer, a thermometer and a condenser. In a typical experiment, TS-1 (40 mg) or Ti-beta (50 mg) was stirred with sulfide (2 mmol), the solvent (10 ml), and H_2O_2 (2 mmol) at a constant temperature. Samples were periodically collected and analyzed by GC in a capillary column (Methyl Silicone Gum, 25 m $\times$ 0.2 mm $\times$ 0.33 μm film thickness). The hydrogen peroxide was measured by standard iodometric titration.

3. Results and discussion

A previous study [13] concerning the oxidation of various alkyl and arylsulfides by H_2O_2 over Ti-beta and TS-1 in alcoholic solvents led us to some interesting remarks:

- the reactivity of thioethers is in agreement with both the nucleophilic character of the sulfur atom (alkylsulfides are more easily oxidized than arylsulfides) and their molecular size: $Et_2S > Pr_2S > Allyl_2S > MePhS > Ph_2S$;
- Ti-beta is more active than TS-1 in the sulfoxidation of hindered molecules;
- an effect of the nature of the alcohol is observed for both TS-1 and Ti-beta: MeOH > t-BuOH.

We present here the results obtained in the study of the sulfoxidation of ethyl sulfide by H_2O_2 in the presence of various solvents. Ethyl sulfide has been chosen as a model molecule in order to avoid steric constraints due to the substrate. Methanol (MeOH), ethanol (EtOH) and t-butanol (t-BuOH) were used as protic solvents, and acetonitrile (MeCN), acetone (MeCOMe) and tetrahydrofuran (THF) were used as aprotic solvents. The concentration of both ethyl sulfide and hydrogen peroxide was 0.19 M in all the solvents, and the reaction temperature was 303 K. The reaction has first

been studied without any catalyst, and then with TS-1 and Ti-beta as catalysts, respectively.

3.1. Ethyl sulfide oxidation by H_2O_2 without catalyst

Fig. 1 shows the ethyl sulfide conversion versus time for all the solvents used, under conditions described above.

The results obtained confirm first that, as already reported [23,24], alkylsulfides can be oxidized with H_2O_2 under mild conditions, even in the absence of any catalyst. Secondly, they show that ethyl sulfide conversion highly depends on the nature of the solvent: the protic solvents, methanol and ethanol, favor the oxidation reaction, whereas, in aprotic solvents acetone and THF, the reaction is very slow.

For each type of solvent (protic and aprotic), a direct correlation between the ethyl sulfide conversion and dielectric constant of the solvents is observed (Table 1), but this correlation is not applicable if we consider all the solvents together: the initial rates obtained for the conversion in acetonitrile and acetone are not as high as it should be, taking into account the high dielectric constant of these solvents compared with those of methanol and ethanol, respectively.

In the case of the protic solvents, the ethyl sulfide conversion is also directly connected to
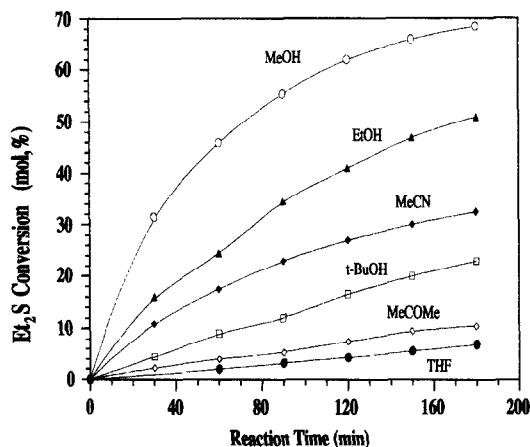
Table 1
Some properties of organic solvents [25] and initial rates for Et_2S oxidation [a]

Solvent	ε [b]	pK_{auto} [c]	$E_T(30)$ [d] (kcal mol^{-1})	$r_0 \times 10^5$ (mol l^{-1} s^{-1})
MeOH	32.66	17.20	55.4	4.80
EtOH	24.55	18.88	51.9	2.27
t-BuOH	12.47	26.80	43.3	0.50
MeCN	35.94		45.6	1.25
MeCOMe	20.56		42.4	0.26
THF	7.58		37.4	0.11

[a] Conditions as in Fig. 1.
[b] Dielectric constant at 25°C.
[c] Autoprotolysis constant at 25°C, according to $2HS = SH_2^+ + S^-$, $K_{auto} = [SH_2^+][S^-]$.
[d] Empirical parameter of solvent polarity from spectroscopic measurements [26,27].

the autoprotolysis constant, K_{auto}, as shown in Table 1 and in agreement with Edwards et al., who found the order $AcOH > H_2O > MeOH > t$-BuOH for the oxidation of thioxane by H_2O_2 at 298 K [24]. A good correlation between the initial rate of the oxidation reaction, r_0, and the molar transition energy is obtained for all the solvents studied. The molar transition energy, $E_T(30)$, is an empirical parameter of the solvent polarity, which is calculated from spectroscopic measurements, according to [26,27]. Fig. 2 shows the linear dependance between log r_0 and this parameter.

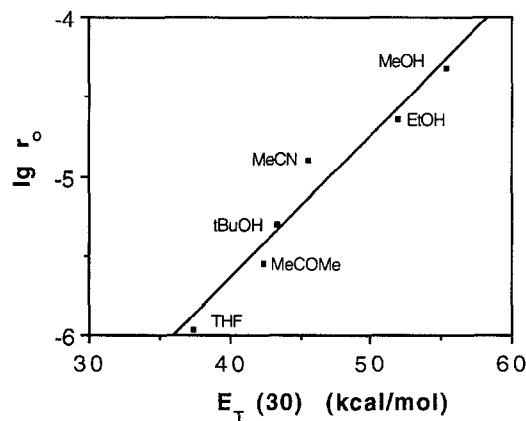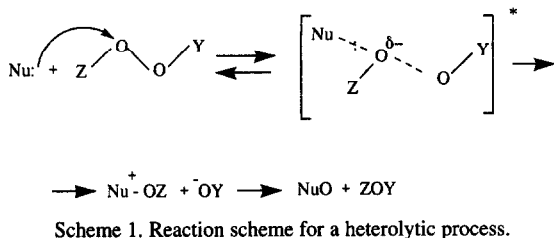These results can be explained if we consider the mechanism of oxidation of organic sub-

Fig. 1. Kinetics of oxidation of Et_2S with H_2O_2 (equimolar ratio) at 303 K; $C_0 = 0.19$ M.

Fig. 2. Correlation between $E_T(30)$ and log r_0 for the oxidation reaction of Et_2S by H_2O_2 at 303 K; $C_0 = 0.19$ M.

Scheme 1. Reaction scheme for a heterolytic process.

Scheme 2. Proposed transition state for Et_2S oxidation with H_2O_2 in alcoholic solvents.

strates by a peroxidic agent ZO–OY. Two mechanisms are possible for the cleavage of the peroxide bond in the oxygen transfer to the organic substrate [28]:
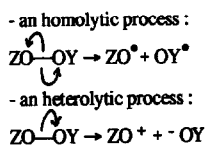
The heterolytic process is energetically favored, particularly in the presence of a nucleophilic reagent (Nu:). In this case, the heterolytic reaction is bimolecular, bringing up a pair of electrons to the oxygen which is losing grip on the O–O bonding electrons (Scheme 1).
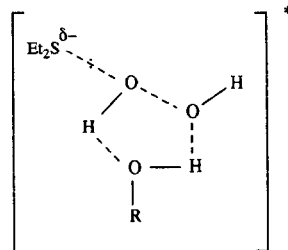
In polar solvents the heterolytic mechanism, possibly aided by structural factors, is certainly the dominant process, where the partially or totally ionic intermediates are stabilized by the solvent. The dependence between the initial rate of the oxidation reaction and a parameter directly connected to the polarity of the solvent confirms such an assumption.

Moreover, if the solvent is hydroxylic (ROH), it may participate, as a third molecule, to the transition state in transferring a proton to the leaving group in a cyclic process [28]. Such a possible transition state for the system Et_2S–H_2O_2 is shown by Scheme 2.

3.2. Ethyl sulfide oxidation by H_2O_2 over Ti-containing zeolites

3.2.1. Catalytic activity

The oxidation of ethyl sulfide by hydrogen peroxide has been carried out, under similar conditions ($C_o = 0.19$ M, $T = 303$ K), using TS-1 and Ti-beta as catalysts, in the same solvents as above. Figs. 3 and 4 show the conversion of ethyl sulfide versus time for TS-1 and Ti-beta respectively.

Fig. 3 shows that the use of TS-1 as catalyst leads to a higher conversion of the thioether, whatever the solvent. The order of efficiency of the solvents is exactly the same as that observed without catalyst: MeOH > EtOH > MeCN > t-BuOH > MeCOMe > THF.

The catalytic activity of Ti-beta (Fig. 4) is higher than that of TS-1 for all the solvents, but the results obtained regarding the behavior of each solvent are significantly different. Thus, it can be seen that, for the three protic solvents, conversions of ethyl sulfide are very similar (MeOH ≈ EtOH ≈ t-BuOH) and much higher than those obtained in aprotic solvents. Such results confirm the proposed mechanism [13] for
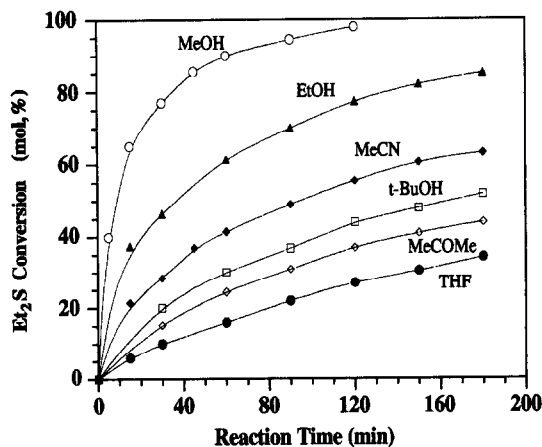

Fig. 3. Kinetics of Et_2S oxidation with H_2O_2 over TS-1 catalyst at 303 K; $C_0 = 0.19$ M.
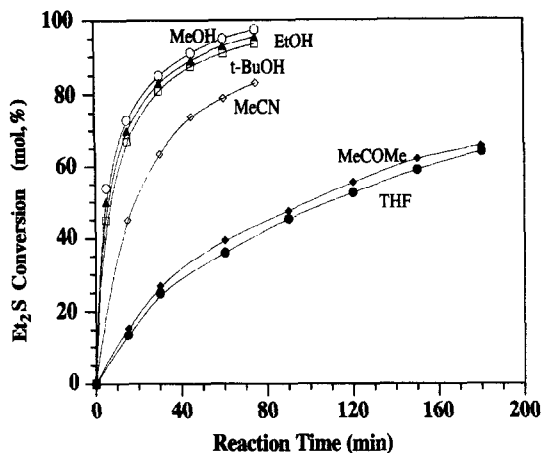
Fig. 4. Kinetics of Et_2S oxidation with H_2O_2 over Ti-beta catalyst at 303 K; $C_0 = 0.19$ M.

the sulfoxidation of thioethers by H_2O_2 catalyzed by Ti-containing zeolites, which involves the coordination of an alcohol molecule to the active titanium site of the hydroperoxo species, as shown in Scheme 3.

It is known that in such a complex the transition metal increases the electrophilicity of the peroxydic oxygen atom, which makes the nucleophilic attack of organic substrate easier. The coordination of a protic solvent to the active site leads to a stabilization of this intermediate, and thus favors this type of mechanism.

The results obtained over the Ti-beta catalyst for ROH type solvents (Fig. 4), i.e. MeOH $\approx$ EtOH $\approx$ t-BuOH, show that, due to the Ti-active species, the influence of the nature of the solvents becomes smaller, compared with the non-catalytic reaction (Fig. 1) where MeOH > EtOH $\gg$ t-BuOH. The latter order of efficiency of alcoholic solvents is found for the oxidation reaction over TS-1 (Fig. 3). Assuming that the oxidation mechanism of ethyl sulfide by H_2O_2
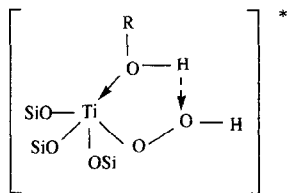
Scheme 3. Proposed active species in oxidation catalyzed by Ti-containing zeolite.

is similar for both TS-1 and Ti-Beta, such results confirm that small pore zeolites, containing Ti, like TS-1, lead to a significant transition-state shape selectivity effect.

If we consider the results obtained over the Ti-beta zeolite in aprotic solvents, Fig. 4 shows a relatively slow conversion of ethyl sulfide in THF and MeCOMe, but a high conversion using MeCN as a solvent. Such a behavior could be explained by a possible addition reaction of hydrogen peroxide to acetonitrile, leading to the peroxyimidic acid, R–C(=NH)–O–O–H, which is known to be an active oxidant agent towards various organic substrates [29–31].

3.2.2. Selectivity

The oxidation of a thioether can yield either the corresponding sulfoxide or sulfone, or both, depending on the reaction conditions (Eq. (1)). For the ethyl sulfide oxidation, the selectivity in ethyl sulfide depends on both the catalyst type (TS-1 < Ti-beta) and the solvent nature MeOH $\approx$ EtOH > MeCN > THF (Table 2).

Moreover, as already observed for the sulfoxidation of various thioethers under the same conditions [13], a fast and high conversion (high r_0) leads to a high selectivity in sulfoxide, as for example in methanol and ethanol.

In order to establish whether the nature of the solvent can modify the rate ratios between the two steps of the sulfoxidation reaction (Eq. (1)) and thus the selectivity, the kinetics of the oxidation reaction of ethyl sulfide has been

Table 2
The initial rate and selectivity in sulfoxide for Et_2S sulfoxidation with H_2O_2 using Ti-containing zeolites [a]

Solvent	$r_0 \times 10^5$ (mol l^{-1} s^{-1})		S_{180} [b] (%)	
	TS-1	Ti-beta	TS-1	Ti-beta
MeOH	25.66	35.00	98.1	98.5
EtOH	9.41	35.50	96.2	98.5
t-BuOH	3.18	29.5	93.8	96.8
MeCN	4.85	11.92	94.7	94.9
MeCOMe	2.13	4.30	93.4	97.2
THF	1.33	3.75	78.2	92.8

[a] $T = 303$ K, $C_0 = 0.19$ M, $Et_2S:H_2O_2 = 1:1$ (mol).
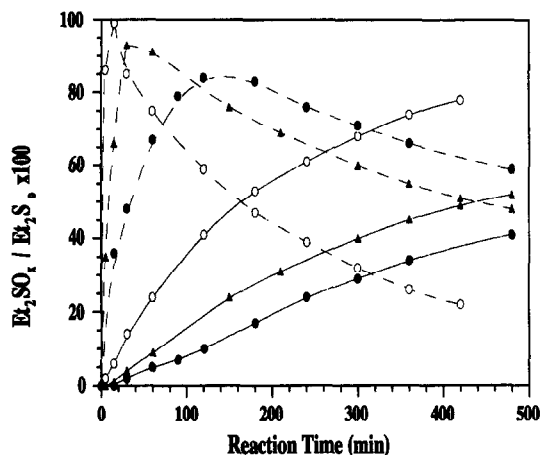[b] $S_{180} = [Et_2SO]/([Et_2SO]+[Et_2SO_2])\times 100$, $t = 180$ min.
[c] $t = 60$ min.

Fig. 5. Kinetics of Et_2S oxidation with an excess (2:1, mol) H_2O_2; catalyst: Ti-beta. (O) EtOH, (▲) MeCN, (●) THF; (– – –) $x = 1$, Et_2SO; (———) $x = 2$, Et_2SO_2.

studied, using an excess of hydrogen peroxide, in ethanol, acetonitrile and tetrahydrofuran as solvents, and over Ti-beta as catalyst (Fig. 5).

The results obtained lead to the following remarks and comments:

1. for a given solvent, the rate of formation of the sulfoxide (dotted lines in Fig. 5) is higher when an excess of H_2O_2 is used compared with the stoichiometric conditions (Fig. 4);

2. as expected, the rate of formation of the sulfone (continuous lines) is lower than that of formation of the sulfoxide (dotted lines), whatever the solvent;

3. the order of efficiency of the solvents is the same for the two steps: EtOH $\gg$ MeCN > THF.

Considering this latter order, the lower selectivity in sulfoxide observed in THF and MeCN compared with EtOH (Table 2) can be attributed only to the lower reaction rate of the first step and not to a favorable effect of these solvents in the second step.

4. Conclusion

The oxidation reaction of ethylsulfide by hydrogen peroxide has been investigated in various organic solvents. It has first been shown

that this reaction can be carried out without catalyst, in mild conditions, and that the reaction rate greatly depends on the nature of the solvent. A linear relation between $\log r_0$ and an empirical parameter of the solvent polarity has been found. Ti-containing zeolites are very active as catalysts for this reaction; in all the solvents used, the activity and selectivity of Ti-beta are higher than those of TS-1. Such a difference is due to a shape-selectivity effect of the medium-pore zeolite TS-1 compared with the large pore structure of Ti-beta. In the case of TS-1, the order of efficiency of the solvents is the same as that observed without catalyst: MeOH > EtOH > MeCN > t-BuOH > MeOMe > THF, whereas, over Ti-beta, the conversion of ethylsulfide is very similar in all the protic solvents, and much higher than that obtained in apotric solvents.

Acknowledgements

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