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Aerobic photochemical oxidation in mesoporous Ti-MCM-41: epoxidation of alkenes and oxidation of sulfides

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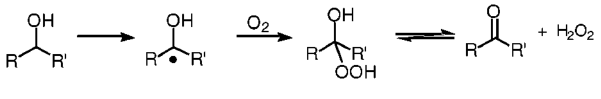
Irradiation with visible light of a secondary alcohol, benzhydrol, in the presence of molecular oxygen within a titanium-substituted mesoporous molecular sieve, Ti-MCM-41, led to the formation of the α-hydroperoxoalcohol and then hydrogen peroxide. The peroxide species reacted *in situ* with alkenes and sulfides and led to the titanium center catalyzed selective formation of epoxides from alkenes and sulfoxides from sulfides. The cascade of reactions represents a new method for the photoactivation of oxygen in the presence of alcohols.

Keywords: epoxidation, photoactivation of molecular oxygen, mesoporous MCM-41

1. Introduction

Synthetic procedures in the area of hydrocarbon oxidation using molecular oxygen as oxygen donor are hampered by severe reaction conditions and/or the radical nature of the reaction that often lead to limited product selectivity. One area of interest in the context of molecular oxygen activation is the *in situ* formation of electrophilic oxidizing species that can be used for the epoxidation of alkenes and sulfoxidation of sulfides [1]. Often, such reactions have been carried out using aldehydes as sacrificial reducing agents. Thus, in the presence of a catalyst or other radical chain initiators, intermediate acylperoxo radicals and/or peracids are formed which lead to alkene epoxidation. Another possibility, examined herein, is (a) to form hydrogen peroxide *in situ* via reaction of an alcohol with molecular oxygen and then (b) to catalytically activate hydrogen peroxide towards epoxidation and sulfoxidation using a high valent (d_0) based catalyst.

Ordinarily, secondary alcohols can react after α-hydrogen abstraction in an autocatalytic cycle with oxygen to yield hydrogen peroxide and ketones [2] through formation of an intermediate α-hydroperoxoalcohol, equation (1), only at elevated temperatures, $>100\,^\circ$C [3].

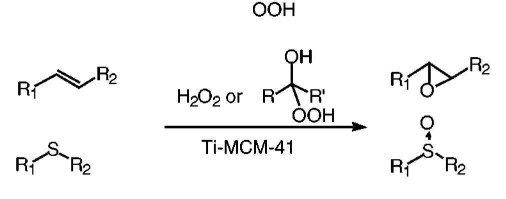


(1)

Recently, in a series of reports, it has been demonstrated that thermal autocatalytic type reactions of alkanes and alkenes can alternatively be carried out photochemically at low temperatures in the confined pores of microporous zeolites [4]. Building on this information, we hypothesized, scheme 1, that using a titanium-substituted mesoporous zeolite, Ti-MCM-41, photochemical activation of a secondary alcohol was also possible and would yield the α-hydroperoxide. The latter could be converted to hydrogen peroxide and ketone. The hydrogen peroxide and/or α-hydroperoxide will then be activated *in situ* at the titanium site in the zeolite [5] towards epoxidation or sulfoxidation.

2. Experimental

All chemicals used were of reagent grade. Alkenes were purified by distillation after passing them over neutral alumina. Ti-MCM-41 was prepared by the known literature procedure [6]. The reaction sequence, as described in scheme 1, was typically evaluated by dissolving 1 mmol diphenylmethanol and 0.7 mmol alkene or sulfide in 1 ml acetonitrile in a 20 ml pyrex glass pressure tube. Then 20 mg Ti-MCM-41 were added and the mixture was magnetically stirred and irradiated with a 150 W mercury lamp under 2 atm O_2 at $60\,^\circ$C for 20 h. The reaction mixtures were analyzed using gas chromatography. Oxidation reaction products were identified using reference standards and GC-MS (HP-5973) equipped with a 30 m × 0.32 mm 5% phenylmethylsilicone (0.25 μm coating) capillary column. Quantification was by GLC (HP 5980) equipped with a flame ionization detector and the same column. ^{1}H NMR measurements were taken on a Bruker AMX-400 spectrometer at 400 MHz.



Scheme 1.

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3. Results and discussion

The results of the epoxidation of alkenes with molecular oxygen in the presence of benzhydrol in Ti-MCM-41 under visible light irradiation are summarized in table 1. An analysis of the results reveals several trends. First, the propensity of alkenes to be autocatalytically oxidized by a free radical pathway was clearly a function in the epoxide product selectivity. Thus, alkenes of lower auto-oxidizability, that is slow rates of propagation in the autooxidation pathway [7] (1-alkene $<$ 2-alkene $<$ cyclooctene; $k_p = 1$, 1.4 and 1.5 $M^{-1}\,s^{-1}$ at 30 °C) selectively yielded the epoxide as the sole product. On the other hand alkenes of higher auto-oxidizability (styrene $>$ 2-methyl-2-heptene; ($k_p = 41$ and 2.5 $M^{-1}\,s^{-1}$ at 30 °C) were considerably less selective in epoxide formation. The reason for this is that as the auto-oxidizability of the alkene increases it becomes comparable to that of the diphenylmethanol ($k_p = 4.8$ $M^{-1}\,s^{-1}$ at 30 °C), so that both form hydroperoxide intermediates [7]. For styrene and 2-methyl-2-heptene, further reaction of the alkene hydroperoxide yields the given by-products. Second, the total yield of the epoxide and the efficiency of the reaction system are proportional to the nucleophilicity of the alkene. As the nucleophilicity increases (1-octene $\approx$ 1-decene $<$ 2-octene $<$ 2-methyl-1-heptene $<$ cyclooctene) [8] the epoxidation reaction with hydrogen peroxide becomes more facile. Furthermore, alcohols of lower auto-oxidizability, such as 2-propanol and 1-phenylethanol were practically unable to initiate the reaction sequence for the epoxidation of 1-alkene. Thus, for the epoxidation of 1-octene, trace amounts ($<$0.01%) of epoxide were formed using 2-propanol and 0.1% epoxide was measured in the presence of 1-phenylethanol. The requirement for titanium in the MCM-41 matrix for epoxidation was unequivocal. A reaction of 1 mmol diphenylmethanol, 0.7 mmol 1-octene, 20 mg MCM-41, 1 ml acetonitrile, 2 atm O_2, 60 °C, 20 h under irradiation by a mercury lamp yielded no epoxide even though 35% of the diphenylmethanol was reacted to benzophenone. Without light there was no conversion of diphenylmethanol or alkene. A similar reaction sequence, scheme 1 was observed for the oxidation of sulfides, table 2. The higher nucleophilicity of sulfides compared to alkenes logically led to higher yields. Aliphatic sulfides were more easily oxidized (higher efficiency) compared to aromatic sulfides although selectivities (sulfoxide/sulfone) were lower due to the higher yields.

Table 1
Photoepoxidation of alkenes catalysed by Ti-MCM-41.[a]

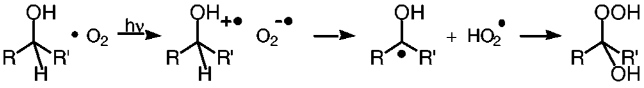
Alkene	Conversion[b]	Efficiency[c]	Selectivity[d]
1-octene	4.5	0.102	1-octeneoxide, 100
2-octene	10.2	0.255	2-octeneoxide, 100
1-decene	4.4	0.096	1-deceneoxide, 100
2-methyl-1-heptene	13.2	0.289	2-methyl-1-hepteneoxide, 100
2-methyl-2-heptene	31.0	0.496[e]	2-methyl-2-hepteneoxide, 80 2-methyl-2-hepten-4-one, 20
Cyclooctene	18.9	0.378	Cycloocteneoxide, 100
Styrene	5.2	0.114[e,f]	Styrene oxide, 11 Phenylacetaldehyde, 8 Benzaldehyde, 81

[a] Reaction conditions: 1 mmol diphenylmethanol, 0.7 mmol alkene, 20 mg Ti-MCM-41, 1 ml acetonitrile, 2 atm O_2, 60 °C, 20 h under irradiation by a mercury lamp.
[b] Total conversion of the alkene.
[c] The efficiency was mole alkene reacted per mole diphenylmethanol reacted; about 30–35% of the diphenylmethanol was reacted to give benzophenone.
[d] mol% given product out of total products.
[e] The efficiency was computed assuming that only the epoxide was formed via the reaction sequence.
[f] The diphenylmethanol conversion was only 3.5%.

Table 2
Photooxidation of sulfides catalysed by Ti-MCM-41.[a]

Sulfide	Conversion[b]	Efficiency[c]	Selectivity[d]
Tetrahydrothiophene	97	0.943	Sulfoxide 90, sulfone 10
Diethylsulfide	96	0.956	Sulfoxide 88, sulfone 12
Thioanisole	77	0.703	Sulfoxide 97, sulfone 3
Thianthrene	6.4	0.063	Mono-sulfoxide 100

[a] Reaction conditions: 1 mmol diphenylmethanol, 0.7 mmol sulfide, 20 mg Ti-MCM-41, 1 ml acetonitrile, 2 atm O_2, 60 °C, 48 h under irradiation by a mercury lamp.
[b] Total conversion of the sulfide.
[c] The efficiency was mole sulfide reacted per mole diphenylmethanol reacted; about 70–77% of the diphenylmethanol was reacted to give benzophenone.
[d] mol% given product out of total products.



Scheme 2.

Some words concerning the reaction mechanism are worth presenting. According to Frei and coworkers [4], visible light photolysis of a alkane/alkene–molecular oxygen complex in a zeolite leads to formation of an excited charge transfer complex followed by formation of hydrocarbon and hydroperoxy radicals. In this case formation of these radicals will lead to the α-hydroperoxy intermediate, scheme 2.

Although the hydroperoxy derivative of diphenylmethanol could be the oxidant [9] activated by Ti-MCM-41 in this system, it is also quite well known that the α-hydroperoxy derivative of diphenylmethanol [2b] tends easily to decompose to benzophenone and hydrogen peroxide. In fact after 1 mmol diphenylmethanol, 0.7 mmol 1-octene, 20 mg MCM-41, 1 ml CD_3CN, and 2 atm O_2 at 60 °C were irradiated for 20 h by a mercury lamp a ^{1}H NMR spectrum of the filtered reaction medium revealed the presence of H_2O_2 at 10.05 ppm compared to a peak at 10.2 ppm for 60% H_2O_2 in CD_3CN. Thus, certainly both the α-hydroperoxoalcohols and hydrogen peroxide are present in the reaction medium. Either or both could be the actual oxidant activated at the titanium site of the Ti-MCM-41.

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References

[1] M.G. Clerici and P. Ingallina, Catal. Today 41 (1998) 351.

[2] (a) G. Strukul, *Catalytic Oxidations with Hydrogen Peroxide as Oxidant* (Kluwer, Dordrecht, 1992);
(b) G. Goor, W. Kunkel and O. Weiberg, in: *Ullman's Encyclopedia of Industrial Chemistry*, 5th Ed., eds. B. Elvers, S. Hawkins, M. Ravenscroft and G. Schulz, (VCH, Weinheim, 1989).

[3] (a) D.L. Vanoppen, D.E. De Vos and P.A. Jacobs, J. Catal. 177 (1998) 22;
(b) J.M. Thomas, R. Raja, G. Sankar and R.G. Bell, Nature 398 (1999) 227;
(c) T. Hayashi, K. Tanaka and M. Haruta, J. Catal. 178 (1998) 566;
(d) T. Mukaiyama and T. Yamada, Bull. Chem. Soc. Jpn. 68 (1995) 17.

[4] (a) F. Blatter, H. Sun, S. Vasenkov and H. Frei, Catal. Today 41 (1998) 297;
(b) H. Sun, F. Blatter and H. Frei, J. Am. Chem. Soc. 118 (1996) 6873;
(c) H. Sun, F. Blatter and H. Frei, J. Am. Chem. Soc. 116 (1994) 7951;
(d) F. Blatter and H. Frei, J. Am. Chem. Soc. 116 (1994) 1812.

[5] (a) B. Notari, Adv. Catal. 41 (1996) 253;
(b) I.W.C.E. Arends, R.A. Sheldon, M. Wallau and U. Schuchardt, Angew. Chem. Int. Ed. Engl. 36 (1997) 1143.

[6] P.T. Tanev, M. Chibwe and T.J. Pinnavaia, Nature 368 (1994) 321.

[7] J.A. Howard, Adv. Free-Radical Chem. 4 (1972) 49.

[8] D. Swern, *Organic Peroxides* (Wiley/Interscience, New York, 1970).

[9] P.A. Ganeshpure and W. Adam, Synthesis (1996) 179.