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# Hydrophobic / hydrophilic effects on the titanium(IV)-catalyzed epoxidation of cyclohexene by tert-alkyl hydroperoxides: 2-methyl-1-phenyl-2-propyl hydroperoxide (MPPH) versus tert-butyl hydroperoxide (TBHP)

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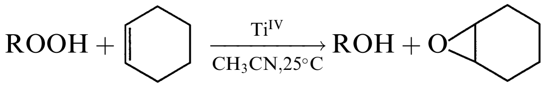
The epoxidation of cyclohexene in acetonitrile under argon at room temperature on a titanium(IV)-containing MCM41 silica catalyst is faster and gives a greater final yield of cyclohexene oxide when the oxygen atom donor is 2-methyl-1-phenyl-2-propyl hydroperoxide (MPPH) than when it is tert-butyl hydroperoxide. This is shown to be due to stronger retardation of the oxidation by tert-butyl alcohol (TBA) than by the alcohol derived from MPPH. The difference in retardation between these two alcohols is attributed to the greater hydrophilicity of TBA. Acetonitrile is a better solvent for this reaction than isooctane, pyridine and a variety of alcohols. These solvent effects are attributed to the hydrophilic nature of the catalyst.

**Keywords:** heterogeneous catalysis, oxidation, product inhibition, silicon, solvent effects, titanium, zeolites

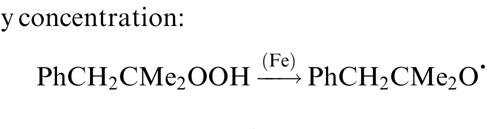
We recently employed two $Ti^{IV}$-containing MCM41 silicas to catalyze the epoxidation of cyclohexene using either tert-butyl hydroperoxide (TBHP) or 2-methyl-1-phenyl-2-propyl hydroperoxide (MPPH) to provide the necessary oxygen atom [1]:



(1)

This work was carried out, in part, to determine whether MPPH could participate in reactions which gave every appearance of being authentic two-electron oxidations. This was important because some of us had made extensive use of MPPH to demonstrate that numerous claims for non-free-radical, two-electron cyclohexane oxidations using TBHP and various iron-based catalysts actually occurred via normal free radical chemistry [2]. The critical steps in the overall cyclohexane oxidation processes actually involve a one-electron oxidation of the hydroperoxide followed by hydrogen atom abstraction from cyclohexane by the tert-butoxyl radical [2]:

$$Me_3COOH \xrightarrow{(Fe)} Me_3CO^{\bullet} \qquad (2)$$



(3)

Similar chemistry is precluded when the TBHP is replaced by MPPH because the alkoxyl radical from the latter hydroperoxide undergoes $\beta$-scission to form the benzyl radical far too rapidly to react with cyclohexane at any concentration:

$$PhCH_2CMe_2OOH \xrightarrow{(Fe)} PhCH_2CMe_2O^{\bullet} \qquad (4)$$

$$PhCH_2CMe_2O^{\bullet} \xrightarrow{\beta} PhCH_2^{\bullet} + Me_2CO \qquad (5)$$

Using MPPH in place of TBHP gave only benzyl radical-derived products and no cyclohexane-derived products [2]. These results led to explicit [3] and implicit [4] suggestions that MPPH was not a competent substitute for TBHP in Fe / hydroperoxide / cyclohexane systems, i.e., in these purported two-electron oxidation processes.

Our experiments with MPPH and cyclohexene using both a catalyst in which the $Ti^{IV}$ was embedded within the walls of the mesoporous silica (Ti → MCM41) and a much more active catalyst in which the $Ti^{IV}$ was grafted on the inner surface of the mesoporous host

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(Ti↑MCM41) showed that MPPH was a very effective (two-electron) epoxidizing agent [1]. Indeed, MPPH gave a two- to three-fold higher yield of cyclohexene oxide after 1 h than did an equal concentration of TBHP [1].

Sheldon and Van Doorn [5] have reported that the epoxidation of 1-octene by a TiO$_2$-on-SiO$_2$ catalyst and TBHP in benzene at 80°C exhibits marked autoretardation. This was attributed to the formation of tert-butanol during the epoxidation process (reaction (1)) since the reaction rate could also be decreased by the deliberate addition of tert-butanol. Although autoretardation was not observed during the epoxidation of cyclohexene under the same conditions, we considered it likely that the enhanced reactivity of MPPH over TBHP was due to differences in the degree of catalyst deactivation by the two alcohols which are co-produced with the epoxide (reaction (1)). The correctness of this supposition was readily demonstrated. Figure 1 shows that the addition of 9.7 equiv. (based on Ti) of 2-methyl-1-phenyl-propan-2-ol (MPPOH, PhCH$_2$CMe$_2$OH) has a slight retarding effect on the Ti↑MCM41 (2.83 wt% Ti and 37.4 wt% Si) catalyzed epoxidation of cyclohexene by TBHP and that the same concentration of tert-butyl alcohol (TBA) has a much greater retarding effect. A similar pattern of retardation was observed upon the addition of 26.4 equiv. (based on Ti) of MPPOH and TBA to the MPPH/cyclohexene/Ti↑MCM41 reaction (see figure 2). The observation that the initial rates of the alcohol inhibited epoxidations were not the same as the rates of the uninhibited reaction at the time when the same amount of alcohol had been produced (i.e., at 9.7 equiv. TBA in figure 1) suggested that it took some time for the alcohol to diffuse into the pores of the catalyst and inhibit the reaction. This was confirmed by stirring the catalyst overnight with 11.3 equiv. TBA which produced much stronger inhibition and an initial rate and growth curve for epoxide formation essentially the same as that for the "uninhibited" reaction from the time of production of 11.3 equiv. TBA (see figure 1).

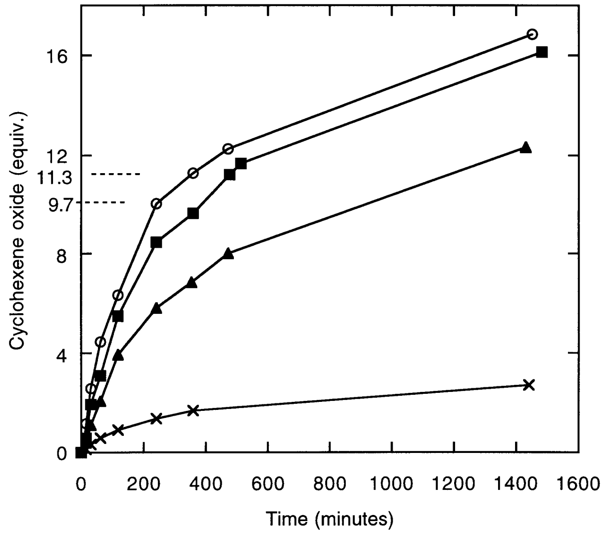

Figure 1. Simultaneously run, matched cyclohexene epoxidations by Ti↑MCM41 and TBHP at room temperature under an atmosphere of argon in acetonitrile containing no added alcohol (○), 9.7 equiv. of TBA (▲), 9.7 equiv. of MPPOH (■), or 11.3 equiv. of TBA (×) which was stirred with the catalyst overnight prior to addition of the TBHP. Experimental procedure as in ref. [1].

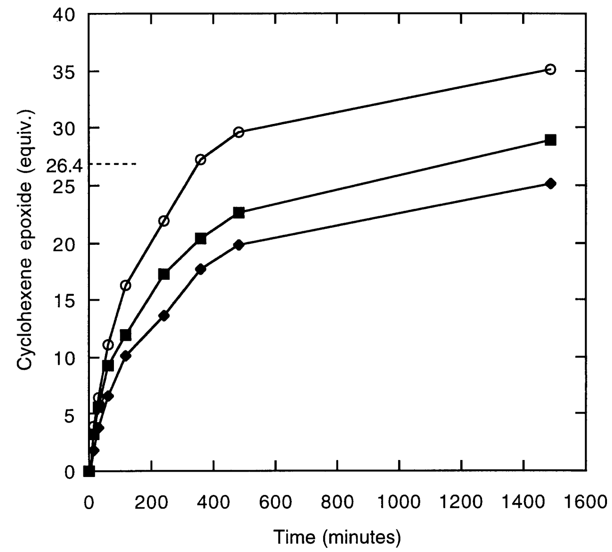

Figure 2. Simultaneously run, matched cyclohexene epoxidations by Ti↑MCM41 and MPPH under an atmosphere of argon at room temperature in acetonitrile containing no added alcohol (○), 26.4 equiv. of TBA (◆) or 26.4 equiv. of MPPOH (■). Experimental procedure as in ref. [1].

Two potential reasons for the stronger catalyst deactivation by TBA relative to MPPH were considered, viz., steric effects and hydrophobic/hydrophilic effects [6,7]. That is, steric hindrance to the coordination of the alcohol to the Ti$^{IV}$ active site [8] on the MCM41 catalyst surface might be lower for TBA than for MPPOH while the greater hydrophilicity of TBA relative to MPPOH would probably tend to hold TBA in the hydrophilic pores of the catalyst after its formation to a greater extent than would be the case for MPPOH.

Tri-tert-butyl carbinol (TTBC) was a very ineffective deactivator of the catalyst relative to MPPOH and TBA (results not shown) which could be attributed either to the steric bulk of this alcohol or to its hydrophobicity, or to both effects. We therefore examined catalyst deactivation by three primary alcohols, ethanol, butan-1-ol and decan-1-ol for which steric hindrance to coordination to the Ti$^{IV}$ should be very similar whereas their hydrophilic character will differ substantially. As can be seen in figure 3 retardation by these alcohols increases from decanol, through butanol, to ethanol. This result is more consistent with alcohol-induced Ti↑MCM41 catalyst deactivation being related to the hydrophilicity of

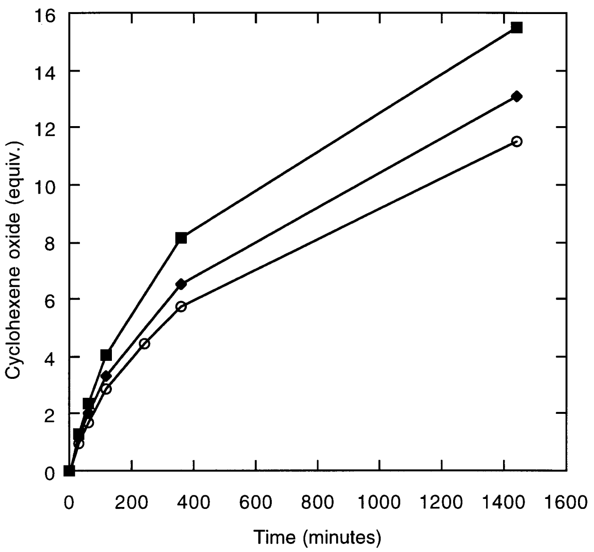

Figure 3. Simultaneously run, matched cyclohexene epoxidations by Ti↑MCM41 and TBHP under an atmosphere of argon at room temperature in acetonitrile containing 11.2 equiv. of ethanol (○), 11.2 equiv. of butan-1-ol (◆) or 11.2 equiv. of decan-1-ol (■). Experimental procedure as in ref. [1].

Table 1
The effect of solvent on cyclohexene epoxidation by Ti↑MCM41 and tert-butyl hydroperoxide [a]

| Solvent | Cyclohexene epoxide (equiv.) | | |
|---|---|---|---|
| | 4 h | 8 h | 24 h |
| acetonitrile | 7.4 | 16 | 21 |
| methanol | 0.0 | 0.094 | 0.44 |
| 2-propanol | 0.004 | 0.17 | 0.28 |
| pyridine | 0.0002 | 0.52 | 1.8 |
| isooctane | 6.7 | 11 | 14 |

[a] Simultaneously run, matched cyclohexene epoxidations by Ti↑MCM41 and TBHP under an atmosphere of argon at room temperature. Experimental procedures as in ref. [1].

the alcohol rather than to its steric requirements. In this respect our results with the Ti↑MCM41 catalyst are congruent with those obtained by Corma et al. [9] when they employed a hydrophilic large-pore Ti-beta zeolite and hydrogen peroxide to epoxidize 1-hexene and found that the rate of epoxidation in acetonitrile was twice that in methanol. In contrast, when they employed a hydrophobic, medium-pore titanium silicate catalyst (TS-1) the epoxidation in methanol was three times as fast as that in acetonitrile.

Our results have two implications for any practical applications of Ti↑MCM41 as an olefin epoxidation catalyst. First, MPPH gives a higher yield of cyclohexene oxide than TBHP because of the differences in hydrophobicity of the corresponding alcohols formed during the reaction, and *not* (apparently) because of any differences in the reactivities of the two tert-alkyl hydroperoxides. Therefore, with this particular catalyst, more efficient epoxidations will be achieved using hydrophobic rather than hydrophilic hydroperoxides. Second, the choice of solvent will be critical, with alcohols being the very worst solvents to employ (see table 1). These results contrast with those of Corma et al. [9] and of Clerici and Ingallina [10] for epoxidations using the TS-1 catalyst for which methanol was the best solvent with activity decreasing in the order MeOH $>$ EtOH $>$ $t$-BuOH.

The ideal solvent for the olefin epoxidation using the Ti↑MCM41 catalyst and tert-alkyl hydroperoxides is one which is not a hydrogen bond donor (HBD) and is also only a relatively poor hydrogen bond acceptor (HBA). If the solvent is a strong HBA it would be expected to deactivate the catalyst (via any surface hydroxyl groups) and also deactivate the hydroperoxide (via ROOH- - -HBA hydrogen bonding). These deductions are supported by the fact that epoxidation was very inefficient in the very good HBA solvent, pyridine (and this was not because the oxidation was "diverted" since pyridine-N-oxide was not detected after 24 h). On the other hand, if the solvent is not a HBA it will only poorly solvate the alcohol formed from the hydroperoxide in the epoxidation process and will therefore tend to "leave" the alcohol in the hydrophilic pores of the catalyst where it will inhibit the reaction. In support of this deduction we note that the yield of cyclohexene oxide was lower in isooctane than acetonitrile. A nice balance between these various solvent requirements is achieved for Ti↑MCM41 by using acetonitrile which may well be the optimum solvent for these epoxidation reactions.

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