Stoichiometry and Kinetics of Gas Phase Cyclohexene Epoxidation by a Silica-Supported tert-Butylperoxidititanium Complex

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INTRODUCTION

Peroxo and alkylperoxo metal complexes are presumed intermediates in the homogeneous and heterogeneous catalytic epoxidations of olefins. Both solid and soluble versions containing high valent, d° transition metal ions activate peroxides heterolytically, thereby facilitating oxygen atom transfer to electron-rich substrates (1). However, mechanistic studies have been undertaken largely with the more readily characterized soluble catalysts (2–4). For heterogeneous catalysts, the fraction of metal sites which participate in selective oxidation is generally unknown. Although measurements and comparisons of overall activity and selectivity are common (5), it is not generally possible to distinguish between mechanisms or measure elementary rate constants for individual sites.

Titanium alkoxides are effective homogeneous catalysts for the epoxidation of substituted olefins. Their propensity for association to multinuclear species is also well-established (6). The active form of a homogeneous, enantioselective titanium-tartrate catalyst was demonstrated to be dinuclear in titanium (7). In contrast, heterogeneous catalysts consisting of titanium embedded in an aluminosilicate framework contain mostly isolated titanium sites (8), although the assertion that such sites are uniquely responsible for catalyst activity is based on
indirect (and disputed) spectroscopic evidence (9). Since the stoichiometry of an epoxidation reaction can be established only if the composition of the active site is known, and since the active site is not necessarily a major (spectroscopically observable) component of a heterogeneous system, there is considerable advantage in mechanistic studies of solid catalysts in which all metal sites have the same or very similar properties.

Grafting of metal complexes onto oxide surfaces can lead to supported catalysts with a high degree of uniformity in the surface organometallic fragments, facilitating the interpretation of kinetic studies. The preparation of solid catalysts by reaction of Ti(O'Pr)₄ with silica has been reported by several groups (10, 11). This material appears to have several desirable properties compared to other heterogeneous Ti/silicate materials, viz., lower moisture-sensitivity and an absence of steric constraint on substrate size (12). Armed with knowledge of the composition of its uniform active sites (13), we now report detailed information about the stoichiometry and kinetics of olefin epoxidation over the solid catalyst.

**EXPERIMENTAL**

**Preparation of Silica-Supported Titanium Catalyst**

The catalyst was prepared by the reaction of Ti(O'Pr)₄ (99.999%, Aldrich) with a non-porous, pyrogenic silica, as described previously (13). Degussa Aerosil™-200 (surface area 183 m²/g) was rehydrated then partially dehydroxylated in vacuo at 200°C, after which treatment the hydroxyl content is reproducible at 2.6 OH/nm² (14). All subsequent manipulations were performed in situ in the absence of inert gases or solvents, using standard breakseal and high vacuum techniques.

Anhydrous tert-butylhydroperoxide (Aldrich, 10 M in decane) was dried over MgSO₄, degassed by three freeze-pump-thaw cycles and stored in a glass bulb under vacuum. Titanium-modified silica pellets or powder were exposed to an excess of 'BuOOH vapor in order to generate the supported tert-butylperoxide complex, followed by evacuation to remove 'PrOH and unreacted 'BuOOH.

**Stoichiometric and Kinetics Measurements**

Cyclohexene was dried and vacuum-distilled before use. It was degassed by three freeze-pump-thaw cycles and stored over activated molecular sieves in a glass bulb. It was introduced into the reactor via vapor phase transfer through a high vacuum manifold (base pressure < 10⁻⁴ Torr). After 30 mins, the epoxide yield was quantified on an HP 6890 GC/MS equipped with a J&W Scientific DB1 capillary column. At the end of each experiment, Ti analysis was performed (15) and epoxide/Ti ratios were calculated. For kinetics experiments, silica powder containing the tert-butylperoxotitanium complex was prepared in an in situ reactor and the reaction initiated by addition of olefin. The IR spectrum of the gas phase above the silica was recorded at timed intervals. Pseudo-first-order rate constants
were extracted from non-linear least-squares fits of the integrated rate equation to the change in absorbance in the v(C=C) region vs. time.

RESULTS AND DISCUSSION

Composition of the Titanium Sites in the Grafted Catalyst

We previously reported the preparation and quantitative characterization of well-defined, uniform titanium alkoxide complexes on a silica surface, via the grafting of Ti(O'Pr)$_4$. We demonstrated, via the mass balance, that the reaction on Aerosil-200 silica pretreated at 200°C results exclusively in the formation of dinuclear oxo-bridged complexes regardless of Ti loading (13), eq 1.

\[
2 =\text{SiOH} + 2 \text{Ti(O'Pr)}_4 \rightarrow (\equiv\text{SiO})_2\text{TiOTi(O'Pr)}_4 + 3 \text{PrOH} + \text{C}_3\text{H}_6 \tag{1}
\]

The dinuclear Ti complex assembles spontaneously on the silica surface via a non-hydrolytic alkoxide condensation reaction which generates the Ti-O-Ti bridge as well as C$_3$H$_6$ (16). Confirmation of this condensation process was obtained via the exposure to Ti(O'Pr)$_4$ of a silica fully loaded (i.e., with no unreacted hydroxyl groups) with a mononuclear titanium alkoxide complex. The latter was prepared by grafting of Ti(NEt$_2$)$_4$ followed by ligand metathesis with PrOH, eq 2. The alkoxide condensation reaction proceeds quantitatively (13), eq 3:

\[
(\equiv\text{SiO})_2\text{Ti(NEt}_2\text{)}_2 + 2 \text{PrOH} \rightarrow (\equiv\text{SiO})_2\text{Ti(O'Pr)}_2 + 2 \text{HNEt}_2 \tag{2}
\]

\[
(\equiv\text{SiO})_2\text{Ti(O'Pr)}_2 + \text{Ti(O'Pr)}_4 \rightarrow (\equiv\text{SiO})_2\text{TiOTi(O'Pr)}_4 + \text{PrOH} + \text{C}_3\text{H}_6 \tag{3}
\]

The 2-propoxide ligands of 1 are displaced quantitatively in the presence of excess tert-butylhydroperoxide, eq 4:

\[
(\equiv\text{SiO})_2\text{TiOTi(O'Pr)}_4 + 4 \text{BuOOH} \rightarrow (\equiv\text{SiO})_2\text{TiOTi(OO'Bu)}_4 + 4 \text{PrOH} \tag{4}
\]

That PrOH is completely displaced from the coordination sphere of Ti, and can be removed from the reaction vessel by simple evacuation, was previously shown by IR experiments involving D-labelling and $^{13}$C CP/MAS NMR (13). The silica-supported Ti complexes remain firmly anchored to the support in the presence of excess tert-butylhydroperoxide vapor: no regeneration of surface hydroxyls (corresponding to protonolysis of the Si-O-Ti linkages (17)) was observed.

Reaction of the Alkylperoxodititanium Complex with Cyclohexene

The dinuclear tert-butylhydroperoxo complex 2 exhibits a vibration at 855 cm$^{-1}$ assigned to v(O-O).[Figure 1a] Upon exposure of 2 to excess cyclohexene vapor at room temperature, this peak disappeared completely, Figure 1b. After reaction of 2
with cyclohexene for 30 mins, cyclohexene oxide was the exclusive volatile product. Upon evacuation to remove physisorbed cyclohexene oxide, the low frequency IR spectrum is qualitatively and quantitatively identical to that of a sample of \((=\text{SiO})_2\text{TiOTi(O'Bu)}_x\), 3, prepared independently by reaction of 1 with tert-butanol.

**Epoxidation Stoichiometry**

Using techniques previously described to quantify gaseous products of surface reactions (13,14), we measured the quantity of epoxide formed by reaction of the tert-butylperoxotitanium complex 2 with an excess of cyclohexene in the absence of tert-butylhydroperoxide (i.e., stoichiometric gas phase reaction conditions). Complex 2, with four tert-butylperoxo ligands per TiOTi unit, generated \((4.11 \pm 0.08)\) equiv. of cyclohexene oxide (average of four experiments), demonstrating that all of its Ti sites are active and all the peroxidic oxygens are utilized. The stoichiometry of the epoxidation can therefore be described precisely, eq 5.

\[
(=\text{SiO})_2\text{TiOTi(O'Bu)}_x + x\text{C}_6\text{H}_{10} \rightarrow (=\text{SiO})_2\text{TiOTi(O'Bu)}_x + 4\text{C}_6\text{H}_{10}O \quad (5)
\]

This finding of complete transfer of peroxidic oxygens to substrate is consistent with IR spectroscopic evidence (Figure 1). Furthermore, regeneration of the tert-butylperoxo complex 2 by treatment of 3 with tert-butylhydroperoxide, followed by its subsequent reaction with cyclohexene, resulted in the formation of another four equiv. of cyclohexene oxide, eq 6. Its active sites are therefore not susceptible to deactivation either during or after epoxidation.

![Figure 1](image_url)  
*Figure 1* Transmission IR spectra of \((=\text{SiO})_2\text{TiOTi(O'Bu)}_x\), 2, (a) before, (b) after reaction with cyclohexene.
Stoichiometric and Kinetic Epoxidations

The rate of epoxidation was measured in situ via the uptake of cyclohexene vapor by the catalyst. At low pressures (ca. 10 Torr), cyclohexene does not adsorb on the unmodified silica surface nor on either of the silica-supported 2-alkoxide complexes 1 and 3. However, the addition of cyclohexene vapor to 2 resulted in a rapid, exponential loss of ν(OC) intensity in the IR spectrum of the gas phase above the silica-supported complex, Figure 2. We infer that epoxidation results in adsorption of cyclohexene oxide on the catalyst surface.

\[
(=\text{SiO})_2\text{TiOTi(OBu)}_4 + \text{tBuOOH} + 4\text{C}_6\text{H}_{10} \rightarrow 4\text{C}_6\text{H}_{10}O \quad (6)
\]

**Kinetics of Epoxidation**

The rate of epoxidation was measured in situ via the uptake of cyclohexene vapor by the catalyst. At low pressures (ca. 10 Torr), cyclohexene does not adsorb on the unmodified silica surface nor on either of the silica-supported 2-alkoxide complexes 1 and 3. However, the addition of cyclohexene vapor to 2 resulted in a rapid, exponential loss of ν(C=C) intensity in the IR spectrum of the gas phase above the silica-supported complex, Figure 2. We infer that epoxidation results in adsorption of cyclohexene oxide on the catalyst surface.

The uptake of cyclohexene by the Ti-modified silica is pseudo-first-order, as shown by the fit to the exponential curve in Figure 2. Furthermore, the measured pseudo-first-order rate constants are linearly dependent on the amount of Ti present in the reactor, Figure 3, consistent with the rate law shown in eq 7:

\[
-k_0 \frac{[\text{C}_6\text{H}_{12}]}{[\text{Ti}]} \approx \frac{d[\text{C}_6\text{H}_{12}]}{dt} = 2k[\text{C}_6\text{H}_{12}][\text{Ti}] \quad (7)
\]

where the factor of 2 arises from the conversion of two equiv. of cyclohexene on each Ti site (see above). The second-order rate constant \(k\) for cyclohexene epoxidation is 8.1 s\(^{-1}\) (mol Ti\(^{-1}\)) at 25°C.
CONCLUSION

Measurement of the stoichiometry of cyclohexene epoxidation over a grafted Ti-silica catalyst demonstrates that (1) all Ti sites are active; and (2) all peroxidic oxygens bound to Ti react. The rate law for the gas-solid reaction is mixed-second-order. Because of the compositional uniformity of the Ti sites and their quantitative participation in the epoxidation reaction, the measured second-order rate constant accurately reflects the activity at each Ti site.

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