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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^0 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 $\text{Ti}(\text{O}^i\text{Pr})_4$ 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 $\text{Ti}(\text{O}^i\text{Pr})_4$ (99.999%, Aldrich) with a non-porous, pyrogenic silica, as described previously (13). Degussa AerosilTM-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 MgSO_4 , 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 ¹BuOOH vapor in order to generate the supported *tert*-butylperoxide complex, followed by evacuation to remove ¹PrOH and unreacted ¹BuOOH.

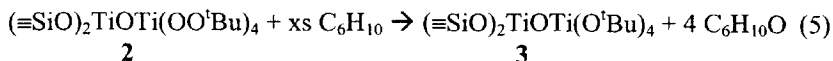
Stoichiometric and Kinetics Measurements

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

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 $(\equiv\text{SiO})_2\text{TiOTi}(\text{O}^t\text{Bu})_4$, **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 ± 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, eq5.



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.

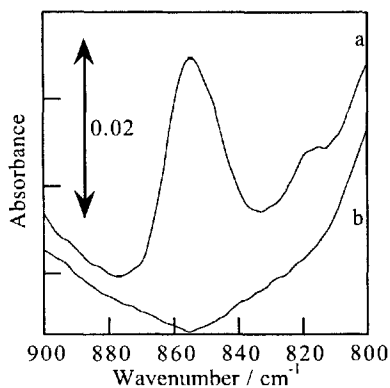


Figure 1 Transmission IR spectra of $(\equiv\text{SiO})_2\text{TiOTi}(\text{OO}^t\text{Bu})_4$, **2**, (a) before, (b) after reaction with cyclohexene.



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 $\nu(\text{C}=\text{C})$ 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.

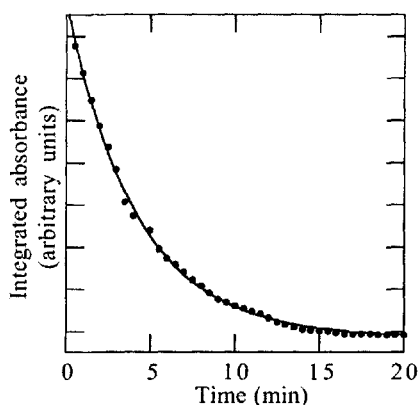


Figure 2 Rate of disappearance of cyclohexene above 2. The solid line is the fit to the first-order rate law.

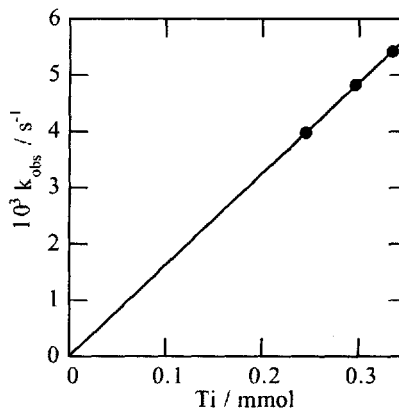


Figure 3 Dependence of pseudo-first-order rate constants for epoxidation of cyclohexene at 25°C on the amount of Ti in 2.

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:

$$-d[\text{C}_6\text{H}_{12}]/dt = 2k[\text{C}_6\text{H}_{12}]n_{\text{Ti}} \quad (7)$$

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 $8.1 \text{ s}^{-1} (\text{mol Ti})^{-1}$ 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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