vation. A crystalline Mn(II) compound was isolated from HF acidified with BF_3, and it was hoped that it was $Mn(FH)_6(BF_4)_2$. In fact it proved to be the ansolvate $Mn(BF_4)_2$ in which seven-coordinate Mn^{2+} is bridged through terminal fluorine atoms of BF_4^- anions in an arrangement in which four of the BF_4^- anions bridge four Mn^{2+} atoms and the remaining three bridge to three Mn^{2+} atoms; i.e., the formula can be written as $Mn(BF_4)_{4/4}(BF_4)_{3/3}$.[10b]

Raman spectroscopy is a technique that could give further evidence for the presence of coordinated HF molecules. The Raman spectrum of Cr^{3+} in AHF did not show any bands that could be associated with Cr–F vibrations. Although disappointing, this is not very surprising. The Cr–F bonds will be fairly ionic in character, and would be expected to give very weak Raman spectra. An indication of the difficulty of detecting Cr–F vibrations can given by experiments on the CrF_6^{3-} ion. In AHF solution no Raman spectrum could be detected, but with a solid sample of $(NH_4)_3CrF_6$, a Raman band was observed at 543 cm^{-1}. This can be reasonably assigned as the totally symmetric A_{1g} Cr–F stretching mode, which is consistent with previous assignments of infrared bands at 535 and 522 cm^{-1} as Cr–F stretching modes.[11]

With Mn^{2+} in AHF, a broad band was observed at 545 cm^{-1} in the Raman spectrum of the most concentrated solution. It is not possible to be certain that this is a Mn–F stretching frequency, but it is in the expected region of the vibrational spectrum. The solid $Mn(BF_4)_2$ has a broad Raman band centered at 532 cm^{-1}, but there are two different types of Mn–F links in this compound and they could both be contributing to the observed band. Overall it can be said the Raman spectra give some evidence for HF coordination, but still more direct evidence is required.

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Registry No. $Cr(FH)_6^{3+}$, 117226-19-4; CrF_6^{3-}, 15276-04-7; $Cr(OH_2)_6^{3-}$, 15276-04-7; $Cr(OH_2)_6^{3+}$, 14873-01-9; Cr^{3+}, 16065-83-1; $Mn(FH)_6^{2+}$, 117226-20-7; MnF_2, 7782-64-1; $Mn(OH_2)_6^{2+}$, 15365-82-9; HF, 7664-39-3.

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Effect of a Clay Support on the Catalytic Epoxidation Activity of a Manganese(III)-Schiff Base Complex

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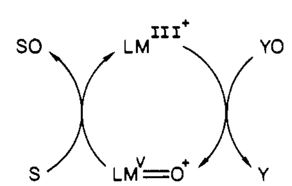
Manganese(III) complexes of porphyrin and Schiff base ligands have attracted considerable interest recently as catalytic oxygen transfer relays.[1,2] Scheme I illustrates the general epoxidation pathway in these systems involving oxidants such as iodosylbenzene,[3] hypochlorites,[4] *p*-cyano-*N*,*N*-dimethylaniline *N*-oxide,[5a] and perhalates.[5b] However, with *tert*-butyl hydroperoxide (TBHP) as the primary oxidant, such catalysts, in the presence of nitrogen bases, catalyze two competing reactions, viz., (a) epoxidation (as in Scheme I) and (b) homolytic decomposition of the hydroperoxide.[6,7] The latter reaction, which leads to the formation of 2-methyl-2-propanol and molecular oxygen, also produces allylic oxidation products of substrates such as cyclohexene via a free-radical chain pathway (Scheme II).[8,9] With a view toward minimizing formation of side products, particularly when TBHP is the oxidant, we have undertaken a systematic study on the effect of heterogenization of $Mn[(salen)(H_2O)]PF_6$ (**4**) on kaolinite clay. Our results indicate an improvement in the epoxidation selectivity upon heterogenization of **4**. A comparative account of the performances of the homogeneous catalyst, **4**, and the heterogeneous catalyst, **5**, is presented herein.

Scheme I



LM = metal-porphyrin or metal-salen complex
salen = [*N*,*N'*-ethylenebis(salicylideneaminato)]
YO = single oxygen donor
S = substrate

Scheme II

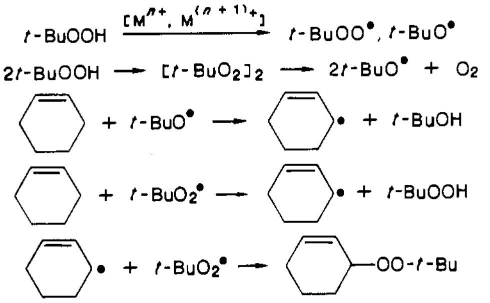


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Table I. Catalyzed Oxidation[a] of Cyclohexene and Cyclooctene by *tert*-Butyl Hydroperoxide

substrate (amt, mmol)	catalyst (amt, mmol)	amt of products, mmol				turnover, [epoxide]/[catalyst]
		epoxide	cyclohexenyl *tert*-butyl peroxide	cyclohexenol	cyclohexenone	
cyclohexene (0.60)	4 (0.011)[b]	0.017[d] (0.013)	0.162	0.007	0.006	1.5[d] (1.2)
	5 (0.011)[c]	0.052[d] (0.049)	0.086	0.006	0.007	4.7[d] (4.4)
cyclooctene (0.60)	4 (0.011)[b]	0.051[d] (0.014)				4.6[d] (1.3)
	5 (0.011)[c]	0.042[d] (0.046)				3.8[d] (4.2)

[a] Conditions: CH_3CN, 5 mL; *tert*-butyl hydroperoxide, 96%, 0.4 mmol; imidazole, 0.132 mmol; ~30 °C; 3 h; all compounds were analyzed by GLC by an internal standard method. [b] Catalyst 4 is $Mn[(salen)(H_2O)]PF_6$. [c] Catalyst 5 is the clay-supported catalyst. The number in parantheses refers to the amount of 4 in mmol adsorbed on the clay matrix. [d] The numbers in parentheses indicate the value obtained in the presence of 2,6-di-*tert*-butyl-4-cresol (0.55 mmol).

Table II. Catalyzed Oxidation[a] of Cyclohexene and Cyclooctene by Iodosylbenzene

substrate (amt, mmol)	catalyst (amt × 10^3, mmol)	[substrate]: [PhIO]: [catalyst]	amt of products, mmol			turnover, [epoxide]/[catalyst]
			epoxide	cyclohexenol	cyclohexenone	
cyclohexene (0.200)	4 (2.0)[b]	100:34:1	0.030	0.002	0.001	15
	5 (2.0)[c]	100:34:1	0.019	0.001	<0.001	10
cyclooctene (0.153)	4 (2.0)[b]	76:34:1	0.039			20
	5 (2.0)[c]	76:34:1	0.029			15

[a] Conditions: CH_3CN, 2 mL; ~30 °C; 45 min; all compounds were analyzed by GLC employing an internal standard method. [b] See footnote *b* in Table I. [c] See footnote *c* in Table I.

Experimental Section

Cyclohex-2-en-1-ol, cyclohex-2-enone and 3-chloroperoxybenzoic acid were commercial samples from Aldrich Chemical Co. Iodosylbenzene,[10] *tert*-butyl cyclohexenyl peroxide,[9] and $Mn[(salen)(H_2O)]PF_6$[7] (4), were prepared by literature procedures. *tert*-Butyl hydroperoxide (70%) was purified by two successive distillations under reduced pressure and found to be 96% pure by iodometric titration.[11] Acetonitrile was a reagent grade commercial solvent repurified by a standard method.[12] Cyclohexene and cyclooctene (Fluka) were distilled over lithium aluminum hydride. All distilled solvents and reagents were stored under nitrogen in Schlenk vessels. The epoxides were independently prepared by the epoxidation of alkenes with 3-chloroperoxybenzoic acid.

Preparation of Clay-Anchored Catalyst (5). To a clear brown solution of 4 (0.240 mmol), in a mixture of acetonitrile (20 mL) and distilled water (20 mL), was added kaolinite claay (10 g) (Hydrite PXS grade, Georgia Kaolin Co.), and the resulting suspension was stirred for 16 h. The clay–catalyst, 5, was then filtered and washed several times with acetonitrile until the UV–visible spectrum of the washings indicated absence of 4. Absorbance measurements at 280 nm of the combined washings showed that 0.138 mmol of catalyst had been adsorbed by the clay.

Epoxidation of Olefins by TBHP and the Analysis of Products. Epoxidations were carried out under nitrogen in a 20-mL Schlenk tube equipped with a stirring bar and a rubber septum. A solution of complex 4 in acetonitrile (2.2×10^{-3} M) was prepared, and 5 mL of this solution (0.011 mmol of catalyst) was placed in a reaction tube filled with nitrogen. To this solution was added 0.132 mmol of imidazole, followed by 0.6 mmol of olefin and 0.05 mmol of *n*-octane (internal standard). Next, tert-butyl hydroperoxide (0.4 mmol) was added dropwise with the aid of a hypodermic syringe, and the GC analysis was performed 30 min after the start of the reactions. For reactions with the clay-supported catalyst 5, 800 mg of clay sample, corresponding to 0.011 mmol of catalyst 4, was used. GC analysis was performed 3 h after the start of the reaction. The rest of the procedure was the same as with 4. Routine organic analyses were carried out by an internal standard method on a Hewlett-Packard 5780A gas chromatograph with a 30-m cross-linked dimethylsilicone capillary column.

Epoxidation of Olefins by PhIO Catalyzed by Catalysts 4 and 5. Epoxidations were carried out under nitrogen in a 20-mL schlenk tube equipped with a magnetic stirring bar and a rubber septum. To a vigorously stirred solution of complex 4 (0.002 mmol in 2 mL of CH_3CN) were added olefin (0.15–0.20 mmol), octane as internal standard (0.10 mmol), and, finally, iodosylbenzene (15 mg, 0.068 mmol). Gas chromatographic analysis was performed by withdrawing aliquots, 45 min after the start of the reactions. When the catalyst is 5, 150 mg of clay sample corresponding to 0.002 mmol of catalyst (4) was used. Quantification of the products was performed as described above.

Results

Comparative data on the epoxidation activities of 4 and 5 with TBHP as the oxidant are presented in Table I. As shown in the table, the yield of cyclohexene oxide is increased ca. 3-fold upon anchoring of 4 in kaolinite, with a concomitant decrease in the yield of the unwanted product, *tert*-butyl cyclohexenyl peroxide. Complete adsorption of the manganese catalyst was confirmed by centrifugation and spectral examination of the supernatant. We note that clay alone does not produce any oxidation products of olefins with TBHP. Also, the amount of cyclohexene oxide formed remained essentially unaltered for both catalysts, when the alkylperoxy radical inhibitor 2,6-di-*tert*-butyl-4-cresol (6) was added to the reaction mixture.

The results differed substantially when cyclooctene was employed as the olefin. In contrast to the results of cyclohexene, the yields of cyclooctene oxide were nearly the same with both 4 and 5. However, addition of radical inhibitor 6 led to a sharp drop in cyclooctene oxide yield with 4 as the catalyst, while no decrease was observed with 5 (Table I). We have also studied the decomposition of TBHP (in the absence of olefin) with 4, 5, and clay alone. We have found that the decomposition of TBHP is slower with 5 than with 4, while little decomposition was observed with clay alone (Figure 1).

The epoxidations were also studied with PhIO as the oxygen donor (Table II). For constant [PhIO], the yields of epoxides are lower with 5 than with 4. Control experiments indicate that the above difference may be ascribed to unproductive decomposition of PhIO to PhI on the clay matrix alone.

Discussion

From the experimental results, it may be seen that catalyst 4 retains its activity upon heterogenization in kaolinate clay. However, qualitative differences are observed in the selectivity of the catalysts toward epoxide formation. Previous results had indicated that, with TBHP as the oxygen donor, epoxidation of cyclohexene by the oxometal-mediated pathway (Scheme I) is accompanied by formation of *tert*-butyl cyclohexenyl peroxide as shown in Scheme II. Since catalyst 5 shows greater selectivity for epoxidation, we hypothesize that side-product formation via Scheme II is less important on our adsorbed catalyst. However, the precise identity of the rate-limiting step involved in decomposition of TBHP on clay is not known.

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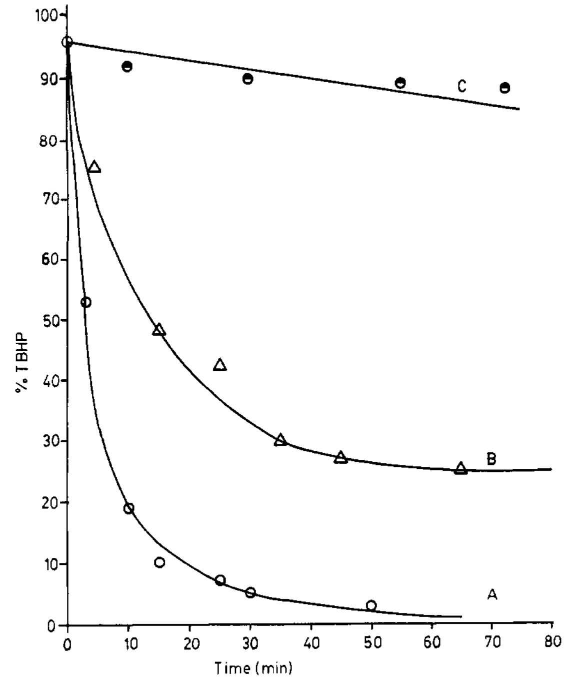
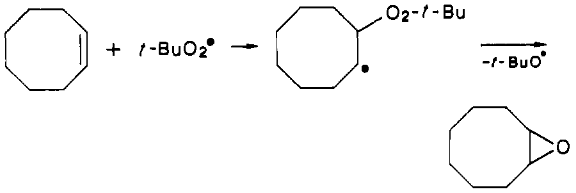


Figure 1. Decomposition of TBHP: (A) in the presence of **4** (2.2×10^{-3} M); (B) in the presence of **5**. (C) in the presence of kaolinite clay. All of the above experiments were carried out with imidazole (0.026 M). The concentration of TBHP was determined iodometrically.

Scheme III



In contrast to the findings with cyclohexene, the cyclooctene oxide formation may occur not only via the oxometal route, but also by a free-radical pathway, which is shown in Scheme III.[13,14] Our results with **4** and **5** indicate nearly identical yields of cyclooctene oxide. To delineate the relative importance of the above pathways with **4** and **5**, experiments were conducted with radical inhibitor **6**. As shown in Table I, addition of the inhibitor led to a sharp drop in epoxide yield with **4**, while no change was observed with **5**. These results therefore suggest that epoxide formation occurs predominantly via the oxometal route with **5**, while the reverse is true with **4**.

In conclusion, the above study has demonstrated that the radical pathway for TBHP decomposition, leading either to side-product formation with cyclohexene or to epoxide formation with cyclooctene, is suppressed on the clay-adsorbed catalyst and that, instead, the oxometal route for epoxidation is the predominant reaction pathway. We note however, that the reactions with **5** are more sluggish than those with **4**. Anchoring of **4** is beneficial when TBHP is the oxidant, while no such advantage accrues with oxidants such as PhIO, which in any case yield epoxides cleanly via the oxometal route.

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Registry No. **4**, 117340-85-9; **6**, 128-37-0; TBHP, 75-91-2; PhIO, 536-80-1; cyclohexene, 110-83-8; cyclooctene, 931-88-4.

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Schiff Base Complex Formation on a Copper Surface Detected by Raman Scattering

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Metal complex formation at a metal surface is a little understood process that is important in such fields as corrosion inhibition and supported heterogeneous catalysis. A major problem is in the identification in situ of the species formed in surface films, which may on occasion be as thin as monolayers. By using surface Raman spectroscopy with a system in which the complex but not the ligand contains a chromophore, we have been able to observe complex formation on a copper surface and observed a subsequent reaction at the surface. In the process we have found behavior that may yet prove of value in investigations of the nature of the enhancement in surface enhanced resonance Raman scattering (SERRS).

Various molecules absorbed on metal surfaces have been observed by using surface enhanced Raman scattering (SERS).[1] There is a molecular specificity resulting from the nature of the metal to adsorbate bond, and the nature of the surface is critical, with some form of surface roughness usually required.[2] This is usually accompanied in solution at an electrode by applying oxidation–reduction cycles (ORC's) to obtain a surface roughened by etching and redepositing metal atoms.[3] The purpose of this roughening appears to be to enable localized surface electron waves to be propagated and to aid in reemission. The natural frequencies of these waves is dependent on the metal, and with visible lasers the effect is more efficient with silver and to a lesser extent copper and gold. Such structured surfaces provide intense scattering that is voltage dependent. From the viewpoint of a chemist, the technique is limited in that the signals depend so heavily on the nature of the surface that many chemical reactions of interest cannot be followed either because during reaction the surface anneals and quenches the SERS signal or because the potentials required for SERS are incompatible with the reaction to be studied.

However, creation of a resonance chromophore on complex formation may enable detection of a Raman signal from a few monolayers due to resonance enhancement even in a wavelength region where the surface would not be expected to be SERS active. Essentially, this resonance is a molecular property and would be expected to be less surface sensitive. It may, in some circumstances, be no more than a molecular resonance. However, in some cases it may be equivalent to the "chemical effect" of the charge-transfer term of SERS,[4,5] and by using radiation in a wavelength range where this effect is not expected to be strong, it may be possible to disentangle these two terms.

Here we report the use of this method to follow the formation of a complex with an aldehyde at a copper/copper oxide surface. We further follow the formation of a Schiff base complex by the addition of *o*-aminophenol to the aldehyde-treated surface. A wavelength of excitation coincident with electronic transitions of the bulk complexes in the blue is used.[6]

A carefully polished and treated copper working electrode was used in a modification of a three-electrode cell described previously.[7] It was cycled five times between 0 and −0.1 V vs SCE

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