Epoxidation reactions with urea–hydrogen peroxide catalyzed by methyltrioxorhenium(VII) on niobia

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Abstract

Soybean oils (oleic, linoleic, and linolenic acids and their methyl esters) are epoxidized readily with urea–hydrogen peroxide (UHP) when methyltrioxorhenium(VII) supported on niobia is used as the catalyst in chloroform. Simple alkenes are epoxidized by the same method. The epoxide and not a diol is produced.
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1. Introduction

The epoxidation of olefins holds sustained interest owing to its practical and theoretical importance. A wide range of catalysts in concert with several stoichiometric oxidizing agents (e.g. O_2, H_2O_2 and *tert*-BuOOH) have been used. Many high-valent metal oxo complexes activate hydrogen peroxide to convert olefins to epoxides [1–4]. Following Herrmann's 1991 discovery that methyltrioxorhenium(VII) is an epoxidation catalyst [5], many scientists have pursued the subject. The goals are improving its reactivity (one means being the addition of a Lewis base such as pyridine) [6–9], its selectivity for epoxide (as opposed to the diol, a frequent and sometimes major by-product) [10,11] and its recoverability and reuse (which is difficult in homogeneous systems). MTO catalysis is based on two peroxo intermediates, $MeRe(O)_2(\kappa^2\text{-}O_2)$ and $MeRe(O)(\kappa^2\text{-}O_2)_2(H_2O)$ [12,13].

In this study we have chosen to use MTO supported on niobia as the catalyst. As the source of hydrogen peroxide, we selected urea–hydrogen peroxide (UHP) [14,15] which is insoluble in chloroform. This heterogeneous catalyst system has been examined with simple olefins. In addition, studies have also been carried out on the epoxidation of the methyl esters of the soybean oils, oleic, linoleic and linolenic acids. The epoxides obtained from them have found a number of practical uses, including as PVC plasticizers. The use of MTO has been described in homogeneous systems [16].

2. Experimental

A literature procedure was followed for the synthesis of $MeReO_3$ [17]. Niobia (325 mesh, Aldrich) was the oxide support. A standard pretreatment procedure [18] was followed to ensure reproducibility. The niobia was calcined overnight at 450 °C under a stream of oxygen ($1.21\,h^{-1}$) to remove surface impurities. After cooling the sample to room temperature, two or

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three small portions of water vapor was introduced in order to generate surface hydroxyl groups. Finally, the niobia was dehydroxylated under dynamic vacuum at 300 °C [18]. MTO (0.5 g, 2 mmol) was introduced onto the surface of 10–20 g of this Nb_2O_5 in either of two ways, by direct sublimation and by placing a toluene solution of MTO in contact with the niobia. The MTO/Nb_2O_5 catalyst was stored in a Schlenk tube under nitrogen. The interaction of the two white solids gives rise to purple-colored material, as reported previously.

The alkenes and UHP were used as received. ^1H NMR spectroscopy was used to monitor alkene conversion and epoxide formation. ^1H and ^{13}C NMR spectra were measured with Varian VXR-300 and Bruker DRX-400 spectrometers.

The rhenium content of the supported catalyst was determined by stirring a weighed quantity of MTO/Nb_2O_5 with 1 M aq. H_2O_2 in 1 M $HClO_4$. This extracts the MTO, converting it quantitatively to $MeRe(O)(\kappa^2\text{-}O_2)_2(H_2O)$ in solution, the concentration of which was determined spectrophotometrically at 360 nm (ε 1.2×10^3 l mol^{-1} cm^{-1}). As prepared by the procedure described, different batches of the catalyst contained 1.2–2 wt.% Re. By itself, UHP does not dissolve in chloroform; insofar as we can determine there is no hydrogen peroxide in solution. When, however, MTO/Nb_2O_5 is added, a faint yellow color in solution develops, indicating a low concentration of a peroxorhenium complex is present in solution. The absorbance of that solution is small, and we have shown (see later) that the solution phase cannot sustain catalysis. The purple MTO/Nb_2O_5 solid turns yellow, indicating that the surface-bound MTO then exists as a peroxo complex. In other words, equilibria between dissolved H_2O_2 and MTO takes place, but now displaced towards the solid phase.

The procedure used in the epoxidation experiments was the following. A limiting amount of the alkene (typically 0.6–2 mmol) was added to a small vial containing 2 ml of $CDCl_3$. A modest excess of UHP (2.5–6.4 mmol) was added along with a weighed amount of MTO/Nb_2O_5 that provided 1–3 mol% of Re per mol of alkene. These mixtures were held at 25 or 50 °C while being stirred for the desired time. After that the solids were removed by filtration with a fine-frit funnel and the NMR spectrum recorded.
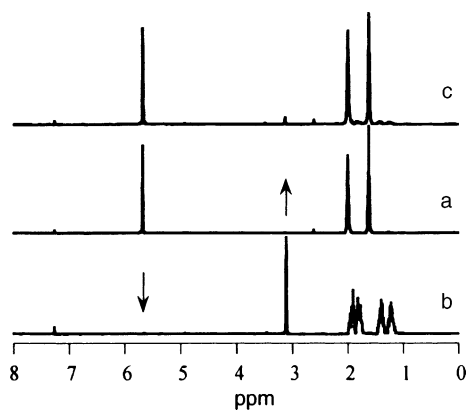

Fig. 1. ^1H NMR spectra taken during the epoxidation of cyclohexene with UHP using the MTO/Nb_2O_5 catalyst in chloroform. (a) At the beginning of the catalytic reaction; (b) at the end of the catalytic reaction; (c) showing the minor amount of reaction that occurs when the liquid phase over the solid catalyst is used (see text).

3. Results and discussion

The utility of ^1H NMR in monitoring the progress of the epoxidation reactions is shown in Fig. 1 by the spectra for two cyclohexene experiments. The signal at the start, Fig. 1a, shows the resonance at δ 5.6 assigned to the olefinic protons. The disappearance of that signal indicates complete epoxidation (Fig. 1b). Concurrent with that, a new resonance was formed at δ 3.1 for the epoxide protons. The degree of epoxidation was calculated by integration of the epoxide resonance.

3.1. Simple alkenes

As carried out under the conditions specified in Table 1, it is evident that the reaction is clean and quantitative. The alkene is entirely absent after the reaction, and the epoxide has been formed quantitatively. The initial studies were conducted at room temperature on the nine cyclic and acyclic alkenes shown in Table 1. The epoxides could be obtained in 70–100% yield in reaction times of 30–100 min. It was apparent to us that each experiment could have been made to proceed quantitatively had a longer time been allowed. The reaction times we found are shorter than those reported previously [19–21].

Table 1
Epoxidation of alkenes with urea–hydrogen peroxide in chloroform catalyzed by methyltrioxorhenium(VII) supported on niobia[a]

	Substrate (mmol)	MTO/Nb$_2$O$_5$ (μmol Re)	UHP (mmol)	Time (min)	Conversion (%)
Cyclohexene	1.97	23	5.92	30	100
	0.98	16	2.0[b]	30	100
4-Methyl-cyclohexene	0.83	17	2.5	30	100
cyclo-Octene	1.52	22	4.56	120	100
trans-Stilbene	0.91	23	2.74	120	100
4-Pentene-1-ol	0.80	16	3.20	120	85
1-Hexene	0.80	16	3.20	120	80
1-Octene	1.60	16	6.40	120	80
3-Hexene	0.64	19	3.20	120	70
1,3-Hexadiene[c]	0.83	19	4.15	120	70

[a] Room temperature.
[b] *tert*-BuOOH in nonane—otherwise the solvent is chloroform.
[c] Epoxidation sites: 45% 3-hexene and 25% 1-hexene.

3.2. Soybean oils

The major effort was devoted to the soybean oils. Early experiments at room temperature took a long time to give high conversions. Reasoning that a process with much bond-breaking is likely to have a high activation energy, we changed the reaction temperature to 50 °C. This provided a satisfactory procedure that gave nearly quantitative yields in 10–30 min with 0.2–2 mol% Re. The ^{1}H NMR data are shown in Fig. 2, and a summary for all three compounds is presented in Table 2. The spectra of the soybean oils and their epoxides match those given in the literature [16,22,23]. In previous studies 30% hydrogen peroxide was used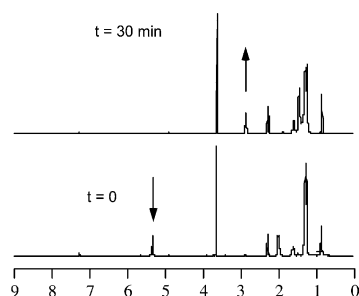 with an added nitrogen base to protect the sensitive epoxides from ring opening [24,25]. This yielded fully-epoxidized product in 7 h. In the present work we can complete the reaction in 30 min at 50 °C when anhydrous UHP was used.

One of the entries in Table 2 shows the results from an experiment with neat methyl oleate (i.e. solvent-free). This gave a quantitative yield of the epoxide after a remarkably short reaction time.

3.3. Effects of water

Experiments were done with added water, 0.1 eq. with respect to cyclohexene. Poor conversions were realized, probably because water lowers the concentration of the active surface-bound peroxorhenium species, as in

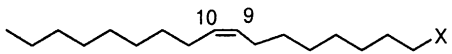$$MeReO_3 + H_2O_2 \rightleftharpoons MeRe(O)_2(\kappa^2\text{-}O_2) + H_2O$$
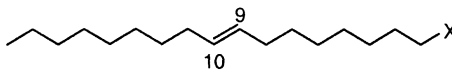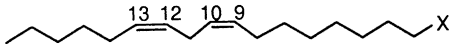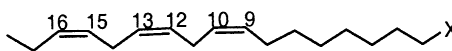
In addition, added water dramatically decreases the epoxidation rate. On the other hand, efforts to remove water by adding 4 Å molecular sieves or anhydrous magnesium sulfate stopped the reaction entirely, just as the molecular sieves stopped homogeneous catalysis by MTO [21].

3.4. Reactions at the surface

We sought to establish that the active catalyst was found at surface-supported sites. The alternative would be that the equilibrium between MTO/Nb$_2$O$_5$(s) had

Fig. 2. Showing the epoxidation of methyl oleate in D$_1$-chloroform at 50 °C under these conditions: 0.3 mmol methyl oleate, 1.2 mmol UHP, 6.0 μmol Re as MTO/Nb$_2$O$_5$.

Table 2
Epoxidation of fatty oils[a] with urea–hydrogen peroxide in chloroform catalyzed by methyltrioxorhenium(VII) supported on niobia at 25 and 50 °C

Soybean oil (X = CO_2H, CO_2CH_3)[a]	X	Substrate (mmol)	MTO/Nb$_2$O$_5$ (μmol)	UHP (mmol)	Time (min)	Yield (%)
oleic acid structure (10 9) —X	CO_2H	3.0[b]	29	12.0	120	100
		3.0[c,d]	6	12.0	10	100
elaidic acid structure (9/10) —X		0.1	6	0.4	20	100
linoleic acid structure (13 12 10 9) —X	CO_2H	0.8[b]	19	3.20	120	90
	CO_2CH_3	3.2[b]	19	12.7	120	95
	CO_2H	0.3[c]	6	1.20	30	100
	CO_2CH_3	3.2	6	12.7	30	100
linolenic acid structure (16 15 13 12 10 9) —X	CO_2H	0.3[b]	19	1.20	120	80
	CO_2CH_3	4.6[c]	6	13.8	30	95

[a] Substrates in order are oleic acid/ester, elaidic acid, linoleic acid/ester, linolenic acid/ester.

[b] 25 °C.

[c] 50 °C.

[d] No solvent.

leached some MTO from the catalyst to form a solution concentration sufficient to carry out the reaction with a homogeneous catalyst. To check this point, duplicate vials of catalyst, UHP and CDCl$_3$ were prepared. One sample was used for the epoxidation of cyclohexene, as usual. The solids were filtered from the other sample and the now-yellow homogeneous solution was used to conduct epoxidation as UHP and cyclohexene were added. Hardly any epoxide was found, as shown in Fig. 1c. This clearly supports the premise that surface-supported MTO is responsible for the catalytic activity.

3.5. Recovery and reuse of the catalyst

Experiments with methyl oleate at higher concentrations than those in Table 2 was carried out; they consisted of using 22 mmol substrate, 33 mmol UHP and 72 μmol Re as MTO/Nb$_2$O$_5$. The reaction went to completion, following which the liquids were removed under vacuum. Additional substrate and UHP in the same amounts were added to residue. The reaction resumed and reached completion in 1 h. The vacuum technique was generally used, but recovery of the catalyst by filtration also was used, and again the epoxidation reaction resumed.

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