



An efficient organic solvent-free methyltrioxorhenium-catalyzed epoxidation of alkenes with hydrogen peroxide

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ARTICLE INFO

Article history:

Received 10 June 2008

Received in revised form 10 July 2008

Accepted 10 July 2008

Available online 16 July 2008

Keywords:

Methyltrioxorhenium
Hydrogen peroxide
Epoxidation
Organic solvent-free

ABSTRACT

Methyltrioxorhenium/3-methylpyrazole has proved to be an efficient catalytic system for epoxidation of alkenes with aqueous 35% H₂O₂ in excellent yields under organic solvent-free conditions. The yields of epoxides by the organic solvent-free epoxidation are comparable to those using CH₂Cl₂ as the organic solvent. The epoxidations of simple alkenes under organic solvent-free conditions are slower than those in CH₂Cl₂, while the epoxidations of alkenols such as citronellol are faster than those in CH₂Cl₂.

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1. Introduction

Epoxides are important compounds for both laboratory and industry as the intermediates and the final products for a wide range of chemicals.^{1,2} Although a major method for producing epoxides in industry is dehydrochlorination of chlorohydrins,² direct epoxidation of alkenes is more favorable than the two-step procedure,³ and extensive studies of direct epoxidation methods have been continued.⁴ Various oxidants have been used for both laboratory and industrial epoxidations. Most of the oxidants are often hazardous and expensive, and in addition, form equimolar amounts of the deoxygenated compounds as waste, which are troublesome to remove from the epoxide products. The ideal alkene epoxidation procedure must be high yield and selectivity without any by-products through a simple and safe operation using a clean and cheap oxidant. In this context, H₂O₂ is one of the ideal oxidants, because of its high atom efficiency (47%) as oxidant and sole theoretical side product water.^{5,6}

Currently, methyltrioxorhenium (CH₃ReO₃, MTO) is one of the most effective catalysts for epoxidation using aqueous H₂O₂.⁷ In 1991, Herrmann and co-workers reported on the H₂O₂ epoxidation of various alkenes using MTO as a catalyst and *t*-BuOH as the solvent under homogeneous reaction medium conditions.⁸ Although catalytic activity of MTO has proven to be very high, the disadvantage of the method is acid (MTO) catalyzed hydrolysis of

epoxides produced during the reaction. Herrmann's group managed modest increases in selectivity by addition of tertiary nitrogen bases.^{8,9} Since then, intense efforts have been made to improve the performance of this significant epoxidation.^{10–17} Subsequently, Sharpless and co-workers found that the addition of 12 mol% pyridine (or substituted pyridines) under organic-aqueous biphasic conditions using CH₂Cl₂ as the organic solvent both suppressed epoxide ring-opening reaction and enhanced catalytic activity.¹⁰ Shortly afterward Herrmann reported pyrazole as a superior additive to pyridine because pyrazole is not affected under the reaction conditions while pyridine is oxidized to pyridine *N*-oxide during epoxidation.¹⁸ Recently, we reported 3-methylpyrazole as a superior additive to pyrazole because MTO/3-methylpyrazole system has higher catalytic activity and longer catalyst lifetime than MTO/pyrazole system.¹⁹

Generally, CH₂Cl₂ has been chosen as the solvent for MTO-catalyzed epoxidation, because fast rate, high yield, and high selectivity are obtained by using CH₂Cl₂.^{10–19} From environmental and toxic points of view, this is certainly not the most appropriate solvent. The negative influences of CH₂Cl₂ on health and the environment²⁰ cancel out the advantages of aqueous H₂O₂. The use of environmentally friendly and lower toxic solvent instead of CH₂Cl₂ or organic solvent-free reaction is desirable. Although various alternative solvents have been investigated to lower the negative impact of CH₂Cl₂, only a limited success has been obtained. The change of the solvent from CH₂Cl₂ to fluorinated alcohols such as trifluoroethanol²¹ and hexafluoro-2-propanol²² allowed reduction of MTO loading. However, acid-sensitive epoxides undergo ring-opening leading to a mixture of compounds in these fluorinated

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alcohols.^{21,22} Room temperature ionic liquids were also examined for MTO-catalyzed epoxidation. A higher MTO loading and use of UHP (urea hydrogen peroxide adduct) were required to obtain comparable results in ionic liquids to those in CH₂Cl₂.²³ Very recently dimethylcarbonate has been reported as the good solvent for MTO-catalyzed oxidations.²⁴ However, the paper reported only one example of alkene epoxidation (styrene) using UHP as the oxidant.

Herein, we wish to report an effective organic solvent-free epoxidation of alkenes with aqueous 35% H₂O₂ catalyzed by MTO using 3-methylpyrazole as an additive when alkenes are liquid. This reaction will be performed under entirely organic solvent-free and halide-free conditions, and avoids the solvent problem.

2. Results and discussion

We first examined organic solvent-free MTO-catalyzed epoxidation of cyclohexene using pyridine,¹⁰ pyrazole,¹⁸ and 3-methylpyrazole¹⁹ as the additives (Table 1). These three additives have been reported to be effective for MTO-catalyzed cyclohexene epoxidation under CH₂Cl₂-aqueous biphasic conditions. Pyridine and 3-methylpyrazole are liquid at room temperature and soluble in cyclohexene. On the other hand, pyrazole is solid at room temperature and insoluble in cyclohexene.

The reaction without additive or organic solvent resulted in hydrolysis of the epoxide produced, and only a trace amount of the epoxide was detected (entry 1).

The epoxidation of cyclohexene with 0.2 mol% MTO in the presence of 10 mol% pyridine, pyrazole, or 3-methylpyrazole in CH₂Cl₂ gave quantitative conversion to cyclohexene oxide (entries 2, 4, and 6).¹⁹

When the epoxidation of cyclohexene was carried out without organic solvent in the presence of pyridine, the reaction stopped within 30 min with large amount of unreacted cyclohexene remained (entry 3). The yellow color of the reaction mixture, which indicates the presence of catalytically active peroxo rhenium species,⁸ changed to colorless within 30 min. This indicated that the decomposition of MTO is rapid in the presence of pyridine under organic solvent-free conditions.^{13c,25–27}

Although pyrazole is not dissolved in common alkenes, aqueous H₂O₂ dissolves pyrazole. When the epoxidations of cyclohexene were carried out without organic solvent in the presence of pyrazole (dissolved in aqueous H₂O₂ before mixing with cyclohexene and MTO), the reaction stopped within 1 h with low conversion of the alkene and low yield of epoxide (entry 5). It is reported that in CH₂Cl₂-aqueous H₂O₂ biphasic system the additive (pyridine) play

an important role as phase-transfer catalyst,^{10d} transporting the peroxy complexes of MTO from the aqueous layer into CH₂Cl₂. Because of the poor solubility of pyrazole in cyclohexene, pyrazole does not work as good phase-transfer catalyst in the cyclohexene-aqueous H₂O₂ biphasic system. This must be the reason of the unsatisfactory result using pyrazole.

When the organic solvent-free epoxidations of cyclohexene were carried out with 3-methylpyrazole, compared with unsatisfactory results using pyridine and pyrazole, a good result was obtained. The reaction completed within 3 h to give 97% yield of cyclohexene oxide (entry 7). Because of the good solubility in cyclohexene, 3-methylpyrazole works as good phase-transfer catalyst in the cyclohexene-aqueous H₂O₂ biphasic system. And furthermore, the lower basicity of 3-methylpyrazole (pK_a=3.3) than pyridine (pK_a=5.2) must prevent the decomposition of MTO.^{10d} These must be the reasons of the excellent result of 3-methylpyrazole as the additive.

The results in Table 1 clearly indicated that 3-methylpyrazole is an effective additive for organic solvent-free epoxidation of alkenes catalyzed by MTO with aqueous H₂O₂ as the terminal oxidant, and that pyridine and pyrazole are ineffective for this purpose.

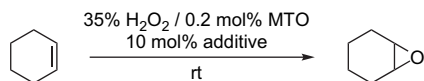
We then investigated the influence of the amount of 3-methylpyrazole added on the cyclohexene epoxidation under organic solvent-free conditions. As can be seen from Figure 1, the efficient epoxidation required 10 mol% or higher amount of 3-methylpyrazole.²⁸ For comparison and general applicability, the amount of 3-methylpyrazole (10 mol%) was maintained for all experiments.

MTO-catalyzed epoxidations of a variety of alkenes using 3-methylpyrazole as an additive under organic solvent-free conditions were examined. The results are summarized in Table 2.

Cyclic alkenes, 1-methylcyclohexene, 1-phenylcyclohexene, cyclopentene, cycloheptene, and cyclooctene, required longer reaction time compared to the reaction in CH₂Cl₂ with comparable conversions and yields of epoxides (entries 1–10).

MTO-catalyzed epoxidation of 1-octene, aliphatic terminal alkene, was slower under organic solvent-free conditions than that

Table 1
MTO-catalyzed epoxidation of cyclohexene with 35% H₂O₂^a



Entry	Additive	Solvent ^b	Time (h)	Conversion ^c (%)	Epoxide ^{c,d} (%)
1	— ^e	— ^f	5	89	<1
2	Pyridine	CH ₂ Cl ₂	5	99	>99
3	Pyridine	— ^f	0.5	14	14
4	Pyrazole	CH ₂ Cl ₂	3	>99	>99
5	Pyrazole	— ^f	1	25	14
6	3-Methylpyrazole	CH ₂ Cl ₂	1	>99	>99
7	3-Methylpyrazole	— ^f	3	>99	97

^a Cyclohexene (20 mmol), 35% H₂O₂ (40 mmol), additive (2 mmol), MTO (0.04 mmol) at room temperature in CH₂Cl₂ (10 mL) or without organic solvent.

^b The results of epoxidation in CH₂Cl₂ are from Ref. 19.

^c Determined by GC analysis.

^d Yield of cyclohexene oxide based on cyclohexene used.

^e Reaction without additive.

^f Reaction without organic solvent.

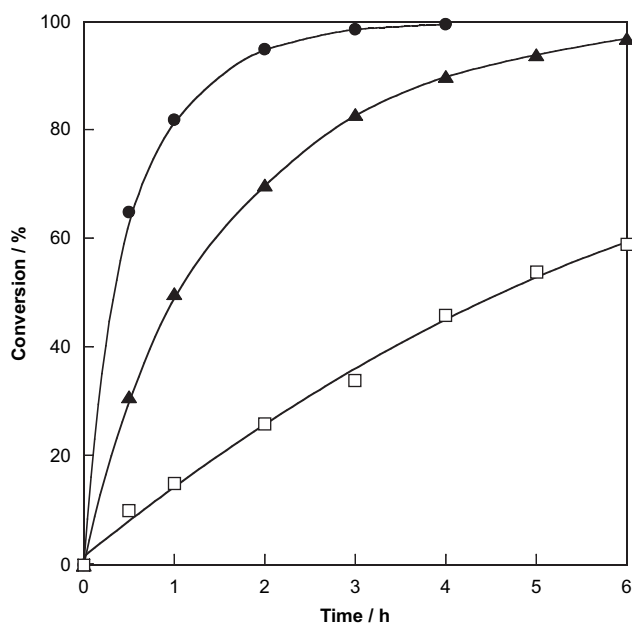


Figure 1. Time course of MTO-catalyzed epoxidation of cyclohexene with different amounts of 3-methylpyrazole under organic solvent-free conditions. Conditions: cyclohexene (10 mmol), 35% H₂O₂ (20 mmol), MTO (0.02 mmol), and 3-methylpyrazole at 20 °C. Analysis by GC: (●) Curve A: 1.5 mmol (15 mol%) 3-methylpyrazole. (▲) Curve B: 1.0 mmol (10 mol%) 3-methylpyrazole. (□) Curve C: 0.5 mmol (5 mol%) 3-methylpyrazole. The curve of 20 mol% 3-methylpyrazole lapped over that of 15 mol%.

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