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# Methyltrioxorhenium/pyrazole—A highly efficient catalyst for the epoxidation of olefins[1]

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**Abstract**

A biphasic system consisting of 35% $H_2O_2$ and methyltrioxorhenium(VII)/pyrazole in $CH_2Cl_2$ catalyzes the epoxidation of a wide range of olefins in excellent yields. Both the reactivity and selectivity of the new catalytic surpasses all known MTO/Lewis base catalysts. The considerable ligand accelerating effect observed here is attributed to the stability of pyrazole against oxidation.

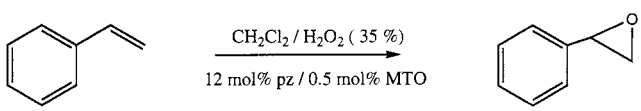

*Keywords:* Methyltrioxorhenium; Olefin Epoxidation; Pyrazole; Catalysis

## 1. Introduction

Since the first reports on the catalytic performance of organorhenium(VII) compounds in 1991 [1–6], a number of studies have shown that methyltrioxorhenium(VII) (MTO, $CH_3ReO_3$) exhibits amazingly high catalytic activities in a variety of organic reactions [7–9]. It was established that MTO forms with $H_2O_2$ a powerful oxidant for a broad range of olefins [3,4,9,10]. While high yields of certain epoxides may be obtained by this procedure, attempts to prepare sensitive epoxides have remained less successful. In particular, 1,2-diols often occur in addition to/or instead of the desired epoxides. In these cases, the employment of Lewis base-ligand e.g. quinuclidine, pyridine (py) and its derivatives proved beneficial for the selectivity [9,11–13]. Here we report on pyrazole (pz) as an oxidation-resistant, thus highly efficient ligand in the MTO-catalyzed olefin epoxidation.

## 2. Results and discussion

Sharpless et al. observed a pyridine-mediated ligand accelerating effect in the epoxidation of cyclooctene by MTO/$H_2O_2$/pyridine, which is specifically pronounced under biphasic conditions [14,15]. An examination of this phenomenon showed that competing processes of olefin epoxidation and *N*-oxidation of the ligand require large excesses of pyridine to maintain high activity levels [16]. A loss of activity due to adduct formation of the catalyst with pyridine *N*-oxide can be compensated to a certain degree by the extraction of pyridine *N*-oxide into the aqueous phase. However, for most starting materials ligand oxidation is much faster than epoxidation of the olefin, resulting in longer reaction times. The use of more oxidation-resistant ligands like 3-cyanopyridine in turn, is limited to less sensitive epoxides, e.g. terminal aliphatic olefins [15].




Scheme 1. Epoxidation of styrene catalyzed by MTO/pyrazole.

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[1] Multiple bonds between transition metals and main-group elements Part 170.

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Table 1
MTO/pyrazole catalyzed epoxidation of olefins

| Entry | Substrate | Time (h) | Conversion (%)[a] (isolated yield) (%)[b] | Selectivity (%)[a] |
|---|---|---|---|---|
| 1 | Styrene | 3 | >99 (93) | >99 |
| 2 | β-*cis*-Methyl styrene | 1 | >99 | >99 |
| 3 | β-*trans*-Methyl styrene | 1 | >99 | >99 |
| 4 | α-Methyl styrene | 1 | >99 (87) | 90 |
| 5 | Cyclohexene | 1 | >99 | >99 |
| 6 | Cyclooctene | 0.02 | 89 | >99 |
| 7 | Cyclopentene | 1 | >99 (92) | >99 |
| 8 | 1-Decene | 14 | >99 | >99 |
| 9 | 1-Hexene | 8 | 95 | >99 |
| 10 | *cis*-Stilbene | 4 | >99 | 92 |
| 11 | *trans*-Stilbene | 4.5 | >99 (90) | 98 |
| 12 | 1,2-Dihydro-naphthalin | 1 | >99 | 95 |

[a] Determined on a 2–4 mmol scale by calibrated GC or $^1$H-NMR;
[b] Determined on a 40 mmol scale.

We now found pyrazole to be a much more suitable ligand for this catalytic process. Scheme 1 shows the exemplified procedure for the epoxidation of styrene catalyzed by MTO/pyrazole in a two-phase system consisting of $CH_2Cl_2$ and aqueous $H_2O_2$.

In a typical run 50 mg of MTO (0.5 mol%) are dissolved in 20 ml $CH_2Cl_2$ and treated with 8 ml of aqueous $H_2O_2$ (two equivalents, 35%). Addition of 330 mg of pyrazole (12 mol%) transfers the catalyst to the organic phase, which can be visually identified by the intense yellow color of the catalytically active peroxorhenium species. The stability of the catalyst is increased by the phase-transfer because hydrolytic decomposition pathways are suppressed [9,14,15]. The reaction is started at room temperature by the addition of the substrate (40 mmol). The work-up procedure consists of phase-separation, decomposition of $H_2O_2$ with catalytic amounts of $MnO_2$, drying over $MgSO_4$ and removal of the solvent. The crude products are purified by distillation under reduced pressure.

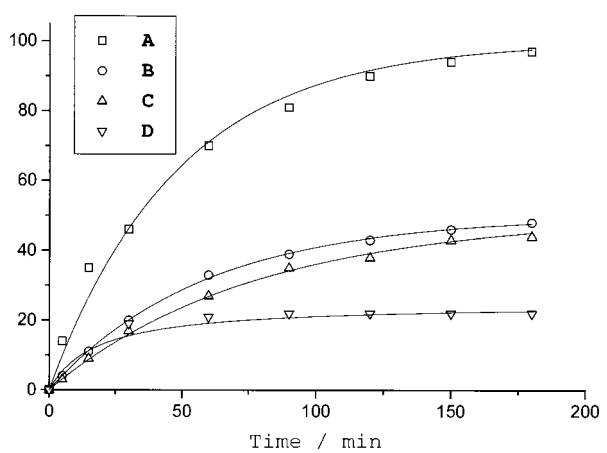


Fig. 1. NMR-monitored comparison of different MTO-catalyst systems under standardized conditions (2 mol $l^{-1}$ styrene in $CDCl_3$, 0.5 mol% MTO); Curve A: MTO/pz (12 mol%)/$H_2O_2$ (aq.); Curve B: MTO/py (12 mol%)/$H_2O_2$ (aq.); Curve C: MTO/py + 3-cyanopy (6 mol% each)/$H_2O_2$ (aq.); Curve D: MTO/$H_2O_2$ (urea adduct).

The catalytic results for a variety of olefins are summarized in Table 1. For all the starting materials hardly any ring-opening or oxidative-cleavage by-products were observed. The epoxides of substituted styrenes are known to be very prone to ring-opening and rearrangement reactions. Even in these cases, selective conversions are achieved by the virtue of MTO/pyrazole. The reaction times are significantly shorter as compared to other MTO-ligand catalysts (see Fig. 1). With this new procedure the entire class of styrene derivatives can be quantitatively converted to their oxides within 1–3 h.

According to GC-experiments the pyrazole is still present after full olefin conversion. The stability of pyrazole against oxidation thus seems to be responsible for the epoxidation efficiency. The catalytically active species is assumed to be a bis(peroxo)rhenium(VII)/pyrazole complex (Fig. 2). Studies towards a detailled understanding of this phenomenon are underway.

The catalyst activity decreases upon reduction of the amount of pyrazole. For example, 6 mol% of pyrazole

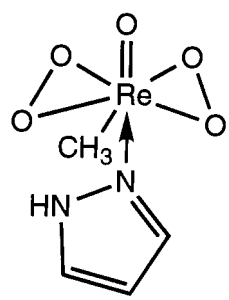


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Fig. 2. Proposed catalytically active species in the MTO/pyrazole catalyzed epoxidation of olefins.

Table 2
MTO/Lewis base catalyzed epoxidation of styrene in 3 h

| Entry | Ligand[b] | Conversion (%)[a] | Selectivity (%)[a] |
|---|---|---|---|
| 1 | Pyrazole | >99 | >99 |
| 2 | Pyrazole (6 mol%) | 90 | 95 |
| 3 | 3-Methyl pyrazole | 71 | >99 |
| 4 | 3,5-Dimethyl pyrazole | 27 | >99 |
| 5 | 2-[3(5)-Pyrazolyl] pyridine | 95 | >99 |
| 6 | 4-Brompyrazole | 92 | 2[c] |
| 7 | — | 89 | 4[c] |

[a] Determined on a 2–4 mmol scale by calibrated GC or $^1$H-NMR;
[b] 0.5 mol% MTO and 12 mol% ligand were employed unless otherwise stated;
[c] Main product: 1-phenyl-1,2-ethanediol (70% selectivity).

only yields 86% styrene oxide after 3 h while the selectivity remains high (>99%). *N*-Alkylated pyrazole derivatives, such as *N*-methyl pyrazole, diminish both the activity and the lifetime of the catalyst. To a lesser degree this remains true also for derivatives with alkyl groups in 3-, and/or 5-position of the pyrazole ring (Table 2). The catalyst systems MTO (without ligand) and MTO/4-bromopyrazole yield similar product distributions (ca. 70% selectivity towards diol).

## 3. Conclusions

The MTO/pyrazole system is the most efficient epoxidation catalyst known to date. Advantages are the easily accessible catalyst, facile procedures, mild conditions, short reaction times, a wide scope of starting materials, and excellent yields. In alignment with the recently introduced possibility of MTO-recycling from exhausted catalyst solutions [17,18], the MTO-catalyzed oxidation of organic substrates now seems open for industrial applications.

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## References

[1] W.A. Herrmann, W. Wagner, U.N. Flessner, U. Volkhardt, H. Komber, Angew. Chem. 103 (1991) 1704.
[2] W.A. Herrmann, W. Wagner, U.N. Flessner, U. Volkhardt, H. Komber, Angew. Chem. Int. Ed. Engl. 30 (1991) 1636.
[3] W.A. Herrmann, R.W. Fischer, D.W. Marz, Angew. Chem. 103 (1991) 1706.
[4] W.A. Herrmann, R.W. Fischer, D.W. Marz, Angew. Chem. Int. Ed. Engl. 30 (1991) 1638.
[5] W.A. Herrmann, M. Wang, Angew. Chem. 103 (1991) 1709.
[6] W.A. Herrmann, M. Wang, Angew. Chem. Int. Ed. Engl. 30 (1991) 1641.
[7] W.A. Herrmann, F.E. Kühn, Acc. Chem. Res. 30 (1997) 169.
[8] B. Schmidt, J. Prakt. Chem. 339 (1997) 439.
[9] W.A. Herrmann, R.W. Fischer, M.U. Rauch, W. Scherer, J. Mol. Catal. 86 (1994) 243.
[10] A.M. Al-Ajlouni, J.H. Espenson, J. Am. Chem. Soc. 117 (1995) 9243.
[11] W. Adam, C.M. Mitchell, Angew. Chem. 108 (1996) 578.
[12] W. Adam, C.M. Mitchell, Angew. Chem. Int. Ed. Engl. 35 (1996) 533.
[13] T.R. Boehlow, C.D. Spilling, Tetrahedron Lett. 37 (1996) 2717.
[14] J. Rudolph, K.L. Reddy, J.P. Chiang, K.B. Sharpless, J. Am. Chem. Soc. 119 (1997) 6189.
[15] C. Copéret, H. Adolfsson, K.B. Sharpless, J. Chem. Soc. Chem. Commun. (1997) 1565.
[16] W.A. Herrmann, H. Ding, R.M. Kratzer, F.E. Kühn, J.J. Haider, R.W. Fischer, J. Organomet. Chem. 549 (1997) 319.
[17] W.A. Herrmann, R.M. Kratzer, R.W. Fischer, Angew. Chem. 109 (1997) 2767.
[18] W.A. Herrmann, R.M. Kratzer, R.W. Fischer, Angew. Chem. Int. Ed. Engl. 36 (1997) 2652.