

Priority Communication

Multiple bonds between transition metals and main-group elements  
Part 168. <sup>1</sup> Methyltrioxorhenium/Lewisbase catalysts in olefin  
epoxidation

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Abstract

Methyltrioxorhenium(VII) (MTO) forms with H<sub>2</sub>O<sub>2</sub> and Lewis bases, e.g., pyridine, a powerful, highly selective oxidant for olefins, both under mono-phase (alcohols as solvents) and biphasic conditions (CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O). Large excess of pyridine is required to maintain the catalytic activity due to rapid oxidation of pyridine to pyridine *N*-oxide, which reaction is catalyzed by MTO, too. The selectivity to epoxides, however, remains high throughout the course of the catalysis, since pyridine *N*-oxide also forms a highly selective but much less active co-catalyst with MTO/H<sub>2</sub>O<sub>2</sub>. Under two-phase conditions, the presence of the aqueous phase ensures high epoxidation activities due to rapid, efficient removal of the pyridine *N*-oxide. © 1997 Elsevier Science S.A.

**Keywords:** Methyltrioxorhenium; Olefins; Pyridine

1. Introduction

Methyltrioxorhenium (MTO) and related organorhenium(VII) oxides are efficient catalysts in a variety of processes [2–4]. One of the first catalytic applications of MTO described in the literature back in 1991 was the epoxidation of olefins using H<sub>2</sub>O<sub>2</sub> as oxidant [5–8]. The selectivity of this process, however, is lowered by the acid-catalyzed ring opening leading to diols. Several improvements of the original procedure have been published to overcome this problem [9–11]. One of the most promising approaches included the addition of Lewis bases, e.g., quinuclidine, pyridine and its derivatives, or *N*-oxides [9–13]. In most cases, it is possible to isolate the complexes formed by the interaction of MTO and the aforesaid Lewis bases [12–16]. It turned out that the employment of Lewis bases in significant excess is beneficial for both *lifetime* and *selectivity* of the cata-

lyst [12,13,17]. This result was confirmed only recently also under two-phase conditions [18,19]. In the latter case, an excess of pyridine even enhances the epoxidation rate as compared to MTO alone [13,18,19]. In the present paper, we unfold results that should help to further improve the olefin epoxidation by means of MTO/Lewis base/H<sub>2</sub>O<sub>2</sub>.

2. Results and discussion

It is well established that the MTO/H<sub>2</sub>O<sub>2</sub> system catalyzes oxidation of amines to amine *N*-oxides [20–24]. Both amine and amine *N*-oxide form catalytically active adducts with the peroxorhenium species [12]. To examine the beneficial aspects of such Lewis base adducts on olefin epoxidation with MTO/H<sub>2</sub>O<sub>2</sub>, we choose pyridine (py) and pyridine *N*-oxide (pyo) as ligands and compared the epoxidation results under homogeneous and heterogeneous conditions. Under two-phase conditions, a 30 wt.% H<sub>2</sub>O<sub>2</sub> solution (aqueous phase) was used as oxidizing agent with CH<sub>2</sub>Cl<sub>2</sub> (GC-studies) or CDCl<sub>3</sub> (NMR studies) as organic phase.

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<sup>1</sup> Part 167, see Ref. [1].

Under homogeneous conditions the reaction was carried out in an anhydrous *tert*-butanol solution of  $\text{H}_2\text{O}_2$  (10%  $\text{H}_2\text{O}_2$ ).

The presence of a catalytically active peroxorhenium species can be visually identified by the distinctive yellow color in solution. In the absence of a Lewis base the catalyst remains in the aqueous phase. Upon addition of pyridine or pyridine *N*-oxide, the catalyst is transferred to the organic phase. These visual observations are confirmed by NMR measurements of each single phase.

Fig. 1 shows a comparison of the epoxidation activities of the two-phase systems MTO/py/ $\text{H}_2\text{O}_2$  (curve A), MTO/ $\text{H}_2\text{O}_2$  (curve B) and MTO/pyo/ $\text{H}_2\text{O}_2$  (curve C). While MTO/py/ $\text{H}_2\text{O}_2$  clearly accelerates the epoxidation of cyclooctene, MTO/pyo/ $\text{H}_2\text{O}_2$  has a detrimental effect on the catalytic activity as compared to the MTO/ $\text{H}_2\text{O}_2$  system. The sigmoidal shape of curve B is presumably caused by phase transfer effects. Since the catalytically active species is in the aqueous phase—as aforesaid—there might be a limitation of mass transport between the two phases under starting conditions.

It is noteworthy that the two-phase MTO/py/ $\text{H}_2\text{O}_2$  system does not show a decrease of catalytic activity during the reaction time despite a considerable amount of pyridine is oxidized to the corresponding *N*-oxide. It should be expected, however, that an increasing excess of pyridine *N*-oxide shifts the coordination equilibrium towards the catalytically less active pyridine *N*-oxide complex. Since both pyridine and pyridine *N*-oxide are soluble in water to a certain degree, we tested the influence of water as a second phase under two-phase conditions in the MTO/ $\text{H}_2\text{O}_2$  system. For this reason, we examined the content of pyridine and pyridine *N*-oxide in both phases applying following strategy.

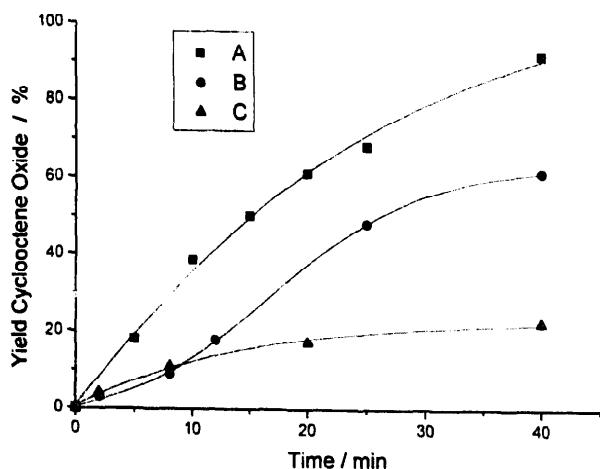


Fig. 1. Comparison of the epoxidation activities of different two-phase systems: MTO/py/ $\text{H}_2\text{O}_2$  (curve A), MTO/ $\text{H}_2\text{O}_2$  (curve B) and MTO/pyo/ $\text{H}_2\text{O}_2$  (curve C).

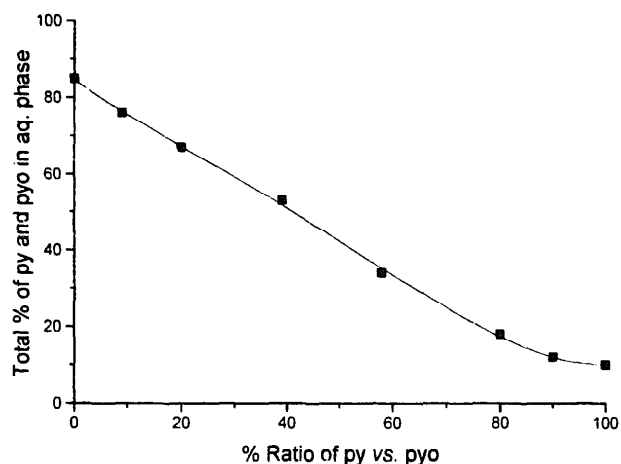


Fig. 2. Extraction degree of pyridine (py) and pyridine *N*-oxide (pyo) at different ratios determined by  $^1\text{H}$  NMR with internal standard (1-decane). A total of 0.5 ml  $\text{CDCl}_3$  was extracted with 0.15 ml distilled water in a NMR tube followed by  $^1\text{H}$  NMR measurement.

(1) The extent of extraction of the pyridine and pyridine *N*-oxide, resp., was studied by a model system involving a series of  $\text{CDCl}_3$  solutions of pyridine and pyridine *N*-oxide at different ratios and concentrations. The amount of each component before and after water extraction was determined by  $^1\text{H}$  NMR using 1-decane as internal standard (Fig. 2).

(2) The extraction coefficients ( $E$ ,  $E = [S]_{\text{org.}}/[S]_{\text{aq.}}$ ) for pure pyridine and pure pyridine *N*-oxide in  $\text{CHCl}_3$  were found to be  $3.0 \pm 0.5$  and  $0.077 \pm 0.005$  resp. They are in good agreement with the results stated in Fig. 2. Therefore, the extraction amount of each species is independent from the py/pyo ratio. At each ratio, ca. 10% of the original amount of pyridine and ca. 80% of the of the pyridine *N*-oxide is extracted into the aqueous phase.

(3) Careful comparison of the amounts of pyridine and pyridine *N*-oxide to the amounts of olefin and epoxide in actual catalytic runs, also monitored by  $^1\text{H}$  NMR spectroscopy confirm the aforesaid results.<sup>2</sup> As mentioned above, the catalyst remains in the organic phase in the presence of pyridine under two-phase conditions. However, the majority of pyridine *N*-oxide generated from pyridine oxidation during the catalysis is rapidly removed from the organic phase because of the big difference in the extraction coefficients of pyridine and pyridine *N*-oxide. This phenomenon keeps the mo-

<sup>2</sup> For a typical run, 25 mg of MTO (0.1 mmol) were dissolved in 10 ml  $\text{CDCl}_3$  in a flask held at room temperature in a water bath. A total of 194  $\mu\text{l}$  (2.4 mmol) pyridine and the substrate (20 mmol) were added and the reaction was started with the addition of  $\text{H}_2\text{O}_2$  (3 ml, 30% aqueous solution, 40 mmol). Samples (ca. 0.3 ml each) were taken, and the epoxidation of olefin and the oxidation of pyridine were monitored by  $^1\text{H}$  NMR.

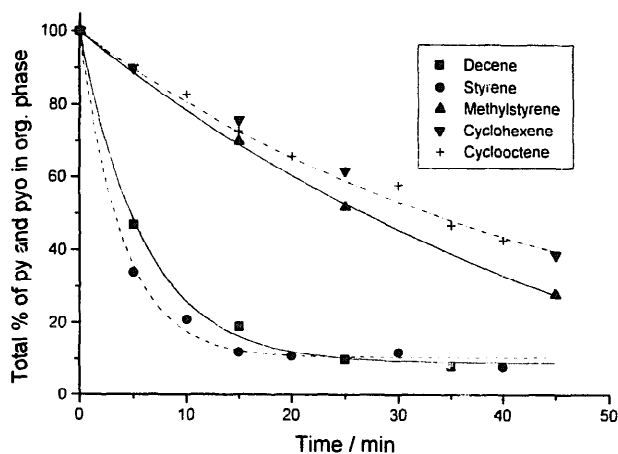


Fig. 3. Decline of the total amount of pyridine and pyridine *N*-oxide under catalytic conditions.

lar ratio pyridine vs. pyridine *N*-oxide high in the organic phase. Therefore, the peroxorhenium catalyst interacts preferably with pyridine, thus ensuring high epoxidation activity.

These observations explain, why even higher concentrations of pyridine in homogeneous systems is required to observe the accelerating effect of this *N*-base. It becomes also clear that—above a certain threshold value—systems with different concentration of pyridine have identical initial catalytic rates. Furthermore, in a two-phase system with the catalyst in the organic phase, the usual decomposition pathway of the catalyst in an aqueous system is not favored [25]. The pyridine helps to keep the catalyst in the stabilizing organic phase resulting in an extended catalyst lifetime.

The chemical nature of the substrates also influences the rate of the pyridine oxidation. Activated olefins, such as cyclooctene, cyclohexene, *cis*-methylstyrene and others, suppress the oxidation of pyridine to some degree.<sup>3</sup> This fact can be observed by comparison of the total percentage of pyridine and pyridine *N*-oxide in the organic phase monitored by *in situ* <sup>1</sup>H NMR (Fig. 3). In case of activated olefins, retarding the pyridine oxidation leads to a slower decline of the (py + pyo)-amount in the organic phase.

Fig. 4 shows the epoxidation of cyclooctene in the presence of pyridine. The amount of pyridine *N*-oxide in the organic phase increases significantly only when almost all cyclooctene is consumed. When the olefin is moderately active (e.g., 1-decene, styrene), the amount of pyridine oxidized to *N*-oxide is significant even in the first few minutes; oxidation of pyridine, thus happens much faster than epoxidation (Fig. 5). In this case, the overall benefit of pyridine addition is to achieve a

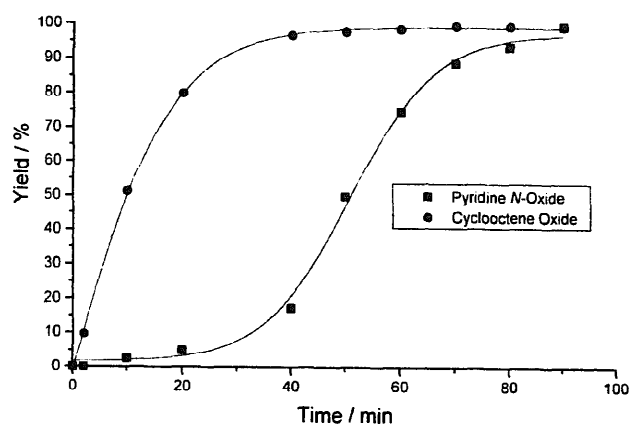


Fig. 4. Epoxidation of cyclooctene in the presence of pyridine under two-phase conditions.

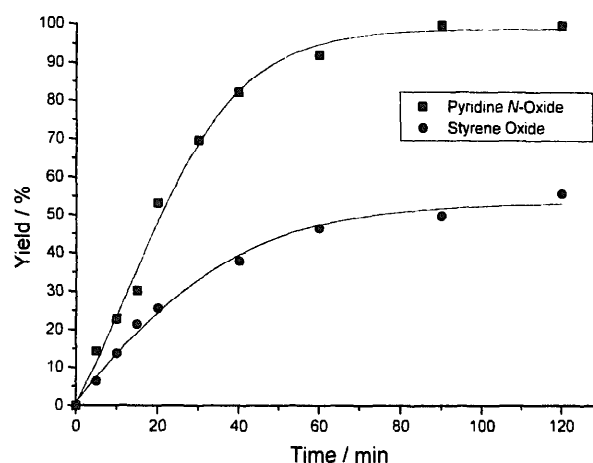


Fig. 5. Epoxidation of styrene in the presence of pyridine under two-phase conditions.

higher selectivity and, to a minor extent, activity. As a matter of fact, using a one-phase system in *tert*-butanol or a two-phase system as described above, has no

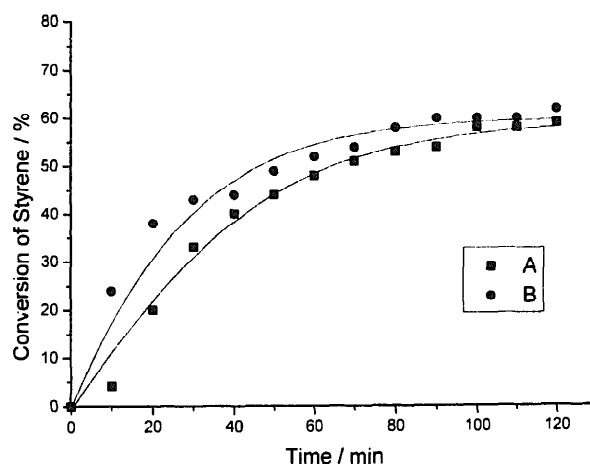


Fig. 6. Comparison of the two-phase system MTO/py/H<sub>2</sub>O<sub>2</sub> (curve A) with the homogeneous system MTO/py/H<sub>2</sub>O<sub>2</sub> (curve B) in *tert*-butanol.

<sup>3</sup> In the absence of olefin, a 12-fold excess of pyridine is completely oxidized within 40 min.

influence on the catalyst activity in the epoxidation of styrene (Fig. 6). But as expected, the selectivity towards epoxides for the MTO/pyH<sub>2</sub>O<sub>2</sub> system remains high throughout the reaction. Compared to the MTO/H<sub>2</sub>O<sub>2</sub> system, only minor amounts of benzaldehyde and 1,2-diol were found.

### 3. Conclusions

MTO/pyridine/H<sub>2</sub>O<sub>2</sub> forms a powerful olefin oxidation system of high activity and selectivity. The competing processes of olefin epoxidation and simultaneous oxidation of the Lewis base ligand requires large excess of pyridine to maintain high activities. 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 under biphasic conditions. This result shows, as in many other cases, the unique but sometimes unexpected advantages of two-phase systems. The nature of olefins also plays an important role influencing the rate of ligand oxidation. Therefore, the overall benefit of *N*-base addition is mainly the high selectivity to epoxides, and in some cases better activity under two-phase conditions. Based on the presented details of the epoxidation catalyzed by the MTO/Lewis base/H<sub>2</sub>O<sub>2</sub> system, a further improvement of activity and selectivity appears possible.

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