

# Catalytic reactions of methylrhenium trioxide on solid oxide supports

Zuolin Zhu, James H. Espenson \*

*Ames Laboratory and Department of Chemistry, Iowa State University, Ames, IA 50011, USA*

Received 2 July 1996; accepted 21 November 1996

## Abstract

Methylrhenium trioxide (MTO), supported on niobia, acts as an effective heterogeneous catalyst for certain chemical reactions. These include reactions of ethyl diazoacetate, which are equivalent to carbene-transfer processes, and selective oxidations that utilize hydrogen peroxide. Both groups of reactions, which are known to occur homogeneously, proceed efficiently and in good yield on the supported catalyst.

*Keywords:* Catalysis; Carbene; Rhenium; Peroxide; Oxidation

## 1. Introduction

Methylrhenium trioxide ( $\text{CH}_3\text{ReO}_3$ , abbreviated as MTO) [1–4] is now well recognized to be an excellent catalyst for a range of reactions. Much effort has been devoted to establishing its effectiveness as a catalyst for oxidations with hydrogen peroxide [5–11] and for establishing the mechanisms of these reactions.

Although MTO shows high reactivity and excellent selectivity in many reactions, and offers the further advantage that rhenium is evidently nontoxic, rhenium is an expensive metal. As useful as the described transformations are, the rhenium is not easy to recover without additional effort. Neither the expense of the rhenium nor the inconvenience of certain recovery procedures will always be of concern if the product is of sufficient value. Nonetheless, the

cost factor cannot be discounted entirely, particularly if an expedient solution can be realized.

We were encouraged by earlier reports that olefin metathesis is catalyzed by MTO supported on silica [2] and on niobia,  $\text{Nb}_2\text{O}_5$  [12]. We have now explored the possibility that MTO on a solid support, silica or niobia, would be more broadly active. The use of an immobilized MTO would not only facilitate the removal of the metal but also its convenient reuse, especially so if the activity of the catalyst is retained throughout. Prior to this study, only sparse reports of the application of supported MTO had appeared. The principal material itself, MTO supported on niobia, has been well characterized [13].

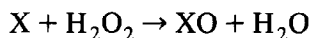
## 2. Results

We have explored whether rhenium supported on a solid oxide will (a) be catalytically

\* Corresponding author.

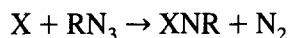
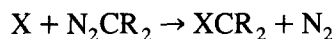
active, (b) be easily recoverable, and (c) retain its reactivity for reuse without further chemical treatment. For our examples, we have chosen several of the reactions cited in the introduction.

In the MTO-catalyzed peroxide reactions an oxygen atom, a 6e fragment, is transferred to the substrate as in the reaction



In this case, the active forms of the catalyst are two:  $MeRe(O_2)O_2$  and  $MeRe(O_2)_2O(H_2O)$ . They are in fairly rapid, but not instantaneous equilibrium with one another and with MTO and hydrogen peroxide [14–16]. In the case of epoxidation reactions ( $X = \text{alkene}$ ), the two show comparable catalytic activity [8,17]. The selective oxidations by MTO are actually quite numerous, as the recent literature attests [4,6,7,9,10,18–26].

More recently, MTO has shown its versatility for other groups of reactions as well. They include carbene transfers from ethyl diazoacetate (EDA) and nitrene transfers from organic azides [27,28]. The transfers of carbenes and nitrenes, other 6e fragments, are shown in these equations



Given the similarities, it is no surprise that MTO is an excellent catalyst for such reactions, some of which have recently been described [28]. Indeed, a considerable body of circumstantial evidence now supports the idea that all three adopt parallel mechanisms. As yet, however, direct documentation is lacking for the intermediates in the latter cases, but the available data suggest that they are analogous to the mono- and diperoxorhenium species which are the catalytically active species in the peroxide reactions. That is to say, an  $\eta^2\text{-(X-O)}$  unit ( $X = NR, CR_2$ ) is implicated [28].

Several groups of nonoxidative organic transformations are also catalyzed by MTO. The coupling-dehydration reactions of alcohols constitute one example [29]. Work as yet unpub-


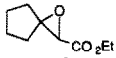

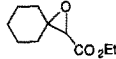
lished describes the catalytic effect of MTO on dioxolane and trioxane formation from carbonyl compounds, on rearrangements of propargylic alcohols, and on Diels–Alder reactions [30].

Experiments were carried out with MTO on silica, the MTO being taken up from toluene solution, and on both niobia and silica, the MTO being deposited by sublimation. MTO on silica is yellow-colored, but we found that the MTO slowly leached off the surface on repeated rinsing with toluene; also, the inherently volatile MTO was lost by heating the sample of MTO on silica under vacuum. On the other hand, the lavender solid formed by the sublimation of MTO onto dried niobia remained unchanged both when the material was rinsed with toluene and ethanol and when it was heated to 100°C. For those reasons, the experiments described here are largely those with niobia-supported MTO. Samples of the supported catalyst were prepared according to the procedures reported in the original work [13].

Supported MTO on niobia has been characterized previously by several spectroscopic methods. They include:  $^{13}C$  MAS NMR ( $\delta$  25 ppm), FTIR, and surface acidity measurements based on pyridine adsorption [13]. In light of this extensive work, we limited ourselves to repeating the FTIR determinations on our samples. They showed peaks at 2990 and 2903  $cm^{-1}$ , compared to the reported 2990 and 2902  $cm^{-1}$ .

It seemed useful to examine a cross-section of the many types of reactions catalyzed by MTO, using a few typical compounds in each category. The processes we selected for this first demonstration of concept are (a) carbene transfer from the intermediate in the MTO-EDA system to protic acceptors—alcohols and amines, (b) carbene transfer to ketones, and (c) oxygen transfer from hydrogen peroxide to nucleophiles — a tertiary amine, a phosphine, and an alkene. The data are summarized in Tables 1 and 2. The products were formed in high yield generally, less so for certain of the peroxide reactions. When a symmetrical alkene was used (Table 2,

Table 1  
Ethyl diazoacetate reactions catalyzed by MTO on niobia

Entry	Substrate	Product	% Yield <sup>a</sup>	Time
1	EtOH	EtOCH <sub>2</sub> CO <sub>2</sub> Et	100 <sup>b</sup>	1 d
2	2-PrOH	2-PrOCH <sub>2</sub> CO <sub>2</sub> Et	100	1 d
3	<i>n</i> -BuOH	<i>n</i> -BuOCH <sub>2</sub> CO <sub>2</sub> Et	100	1 d
4	PhNH <sub>2</sub>	PhNHCH <sub>2</sub> CO <sub>2</sub> Et	~95	1 d
5	<i>n</i> -C <sub>6</sub> H <sub>13</sub> NH <sub>2</sub>	<i>n</i> -C <sub>6</sub> H <sub>13</sub> NHCH <sub>2</sub> CO <sub>2</sub> Et	~90	1 d
6	PhCH(CH <sub>3</sub> )NH <sub>2</sub>	PhCH(CH <sub>3</sub> )NHCH <sub>2</sub> CO <sub>2</sub> Et	~90	1 d
7			>95 <sup>c</sup>	1 d
8			>97 <sup>d</sup>	1 d

<sup>a</sup> Based on EDA; the same reactions run homogeneously are given in Ref. [28]. The substrate itself was the solvent. Either way, the yields were nearly quantitative.

<sup>b</sup> The same reaction on silica gel gave 100% of EtOCH<sub>2</sub>CO<sub>2</sub>Et after one day, and the catalyst was still yellow; after one more day, however, the yellow color had disappeared, signifying catalyst deactivation.

<sup>c</sup> <sup>1</sup>H-NMR: 1.28 (t, 3H), 1.72–2.42 (m, 8H), 4.16 (s, 1H), 4.21 ppm (q, 2H); <sup>13</sup>C-NMR: 14.00, 22.86, 34.64, 60.65, 60.68, 61.17, and 170.35 ppm.

<sup>d</sup> <sup>1</sup>H-NMR: 1.27 (t, 3H), 1.53–2.55 (m, 10H), 4.15 (s, 1H), 4.20 ppm (q, 2H); <sup>13</sup>C-NMR: 13.86, 24.82, 35.43, 60.66, 60.70, 61.16, 170.41 ppm.

entry 3), epoxidation took place as expected, along with an accompanying degree of epoxide ring-opening. The second process was also catalyzed by the MTO/H<sub>2</sub>O<sub>2</sub> system.

On the other hand, the use of an unsymmetric alkene, entry 4, resulted in a diol that clearly arose from the epoxidation and ring opening of the symmetric alkene from the prior metathesis of the starting material [2,12]. From this, we conclude that metathesis is faster than epoxidation on MTO/Nb<sub>2</sub>O<sub>5</sub>. The supported catalyst does not exhibit the induction period often found for homogeneous reactions of ethyl diazoacetate. One further reaction type was attempted: condensation of Ph<sub>2</sub>CHOH to the ether. This was the least satisfactory of all, giving 10% yield only.


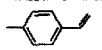
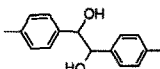

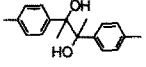
To demonstrate one of our major theses, that the supported catalyst can be recovered and reused, the experiment with excess ethanol and

EDA (Table 1, entry 1) was repeated. A second 1 mL portion of EDA was added; the reaction resumed and was completed in 20 h. This is about the same time as before. Diethyl fumarate and diethyl maleate, side products from the same reaction run homogeneously, were not detected when MTO on niobia was used.

Additionally, the catalyst used in one reaction, that between 2-PrOH and EDA, was separated after the reaction was complete, rinsed with ethanol, and then used to conduct a different reaction, that between EtOH and EDA. The product, EtOCH<sub>2</sub>CO<sub>2</sub>Et, was again formed quantitatively in 24 h, just as when fresh catalyst was employed. These findings demonstrate the potential of this method.

A further control was carried out to show that Nb<sub>2</sub>O<sub>5</sub> itself, without the adsorption of MTO, is unable to serve as a catalyst. Two reactions, EtOH + EDA and PhC(CH<sub>3</sub>)CH<sub>2</sub> + H<sub>2</sub>O<sub>2</sub>, were used as the blanks.

Table 2  
Products and product yields from organic transformations with hydrogen peroxide catalyzed by methylrhenium trioxide supported on niobia

Entry	Substrate	Product	% Yield <sup>a</sup>	Time
1	PhNMe <sub>2</sub>	PhN(O)Me <sub>2</sub>	40	2 d
2	Ph <sub>3</sub> P	Ph <sub>3</sub> P=O	100	4 h
3	trans- PhCH=CHPh		90 <sup>b</sup>	
4			95 <sup>c,d</sup>	2 d
5			80 <sup>d</sup>	2 d

<sup>a</sup> Except as noted, acetone was the solvent.

<sup>b</sup> This reaction was carried out in acetic acid–acetone (100:40) to provide for proper solubility. The balance of the products consisted of *cis*-stilbene oxide (5%) and hydrobenzoin (5%). No gas was liberated.

<sup>c</sup> Two isomers in 4:1 ratio were obtained, the major one with a <sup>1</sup>H-NMR spectrum at 2.09 (s), 4.22 (s), and 7.18 (m) ppm. The other gave resonances at 2.33 (s), 4.90 (s), and 7.22 (m) ppm.

<sup>d</sup> Gas formation (C<sub>2</sub>H<sub>4</sub>) shows that olefin metathesis preceded oxidation. Propylene was also formed from C<sub>2</sub>Me<sub>4</sub> under these conditions.

The reactions reported here constitute a representative sample of those that are possible with this heterogeneous catalyst system. Work is in progress to extend the applications of MTO on niobia to systems in which the homogeneous catalyst is inclined to decomposition [31].

The nature of the catalyst–surface interaction has not been fully established. We conjecture that the never-quite-dry oxide surface contains Nb–OH groups that can condense with one (and likely two) Re=O groups to fix the MTO firmly to the oxide surface. This leaves another Re=O group free to interact with H<sub>2</sub>O<sub>2</sub> or N<sub>2</sub>CHCO<sub>2</sub>Et to produce the catalytically active intermediates (i.e., the  $\eta^2$ -O<sub>2</sub>Re group and its carbene analog), that are known to be involved in the homogeneous catalytic chemistry. Whether a monoperoxo- or a diperoxorhenium species is the active form cannot be stated with certainty, but the presence of an  $\eta^2$ -O<sub>2</sub>Re group is indicated by the fully-consistent picture of the mechanisms of all the homogeneous reactions.

### 3. Experimental section

The supported catalyst was prepared according to the literature procedure [13]. The niobia sample (325 mesh, Aldrich) was calcined overnight at 450°C under a stream of oxygen (1.2 L h<sup>-1</sup>); after cooling to room temperature and evacuation, it was exposed to water vapor in a desiccator for 4 h, then evacuated to 300°C overnight [12,13,32]. MTO (0.5 g, 2 mmol) was sublimed onto the surface of 25 g of this niobium oxide. For other experiments, silica gel was heated for 1 h at 550°C in a stream of nitrogen, and then doped with MTO in toluene after it had been cooled to room temperature.

The reactions of ethyl diazoacetate (Table 1) were carried out by adding EDA (1 mL, 9 mmol) to 15 mL of the neat substrate, which was used as the solvent. This mixture was stirred with 0.5–2.5 g MTO/Nb<sub>2</sub>O<sub>5</sub> (0.04–0.2 mmol MTO) for  $\leq$  24 h. In Table 2, the substrate (1 mmol), peroxide (10 mmol), and 0.5 g

MTO/Nb<sub>2</sub>O<sub>5</sub> (10 mg MTO, 0.04 mmol) were stirred in 15 mL glacial acetic acid for 4 h – 1 d, as needed. Benzhydrol (1 mmol) with 1 g MTO/Nb<sub>2</sub>O<sub>5</sub> (0.1 mmol MTO) were stirred in 20 mL CHCl<sub>3</sub> for 1 d; no improvement in yield was noted at longer times, as the catalyst had decomposed.

The product yields were determined from the isolated yields, except when they approached 100%, in which case GC-MS was used to establish the quantitative yield.

### Acknowledgements

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract W-7405-Eng-82.

### References

- [1] I.R. Beattie and P.J. Jones, *Inorg. Chem.* 18 (1979) 2318.
- [2] W.A. Herrmann, J.G. Kuchler, J.K. Felixberger, E. Herdtweck and W. Wagner, *Anal. Chem.* 27 (1988) 394.
- [3] W.A. Herrmann, F.E. Kühn, R.W. Fischer, W.R. Thiel and C.C. Romão, *Inorg. Chem.* 31 (1992) 4431.
- [4] W.A. Herrmann, R.W. Fischer and D.W. Marz, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 1638.
- [5] P. Huston, J.H. Espenson and A. Bakac, *Inorg. Chem.* 32 (1993) 4517.
- [6] K.A. Vassell and J.H. Espenson, *Inorg. Chem.* 33 (1994) 5491.
- [7] W.A. Herrmann, R.W. Fischer, M.U. Rauch and W. Scherer, *J. Mol. Catal.* 86 (1994) 243.
- [8] A. Al-Ajlouni and J.H. Espenson, *J. Am. Chem. Soc.* 117 (1995) 9243.
- [9] M.M. Abu-Omar and J.H. Espenson, *J. Am. Chem. Soc.* 117 (1995) 272.
- [10] Z. Zhu and J.H. Espenson, *J. Org. Chem.* 60 (1995) 1326.
- [11] W. Adam, W.A. Herrmann, C.R. Saha-Moller and M. Shimizu, *J. Mol. Catal.* 97 (1995) 15.
- [12] R. Buffon, A. Choplin, M. Leconte, J.-M. Basset, R. Touroude and W.A. Herrmann, *J. Mol. Catal.* 72 (1992) L7.
- [13] R. Buffon, A. Auroux, F. Lefebvre, M. Leconte, A. Choplin, J.-M. Basset and W.A. Herrmann, *J. Mol. Catal.* 76 (1992) 287.
- [14] S. Yamazaki, J.H. Espenson and P. Huston, *Inorg. Chem.* 32 (1993) 4683.
- [15] O. Pestovsky, R. vanEldik, P. Huston and J.H. Espenson, *J. Chem. Soc. Dalton Trans.* (1995) 133.

- [16] P.J. Hansen and J.H. Espenson, *Inorg. Chem.* 34 (1995) 5839.
- [17] A. Al-Ajlouni and J.H. Espenson, *J. Org. Chem.* 61 (1996) 3969.
- [18] W. Adam, W.A. Herrmann, J. Lin and C.R. Saha-Mölller, *J. Org. Chem.* 59 (1994) 8281.
- [19] W. Adam, C.M. Mitchell and C.R. Saha-Moller, *Tetrahedron* 50 (1994) 13121.
- [20] W. Adam and C.M. Mitchell, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 533.
- [21] K.N. Brown and J.H. Espenson, *Inorg. Chem.* 35 (1996) 7211.
- [22] W.A. Herrmann, R.W. Fischer, W. Scherer and M.U. Rauch, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 1157.
- [23] W.A. Herrmann, R.W. Fischer and J.D.G. Correia, *J. Mol. Catal.* 94 (1994) 213.
- [24] E.I. Karasevich, A.V. Nikitin and V.L. Rubailo, *Kinet. Catal.* 35 (1994) 810.
- [25] R.W. Murray, K. Iyanar, J. Chen and J.T. Wearing, *Tetrahedron Lett.* 36 (1995) 6415.
- [26] Z. Zhu and J.H. Espenson, *J. Org. Chem.* 60 (1995) 7727.
- [27] Z. Zhu and J.H. Espenson, *J. Org. Chem.* 60 (1995) 7090.
- [28] Z. Zhu and J.H. Espenson, *J. Am. Chem. Soc.* 118 (1996) 9901.
- [29] Z. Zhu and J.H. Espenson, *J. Org. Chem.* 61 (1996) 324.
- [30] Z. Zhu, J. Jacob and J.H. Espenson, unpublished information.
- [31] M.M. Abu-Omar, P.J. Hansen and J.H. Espenson, *J. Am. Chem. Soc.* 118 (1996) 4966.
- [32] W.A. Herrmann, W. Wagner, U.N. Flessner, U. Volkhardt and H. Komber, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 1636.