

Mechanistic Details to Facilitate Applications of an Exceptional Catalyst, Methyltrioxorhenium: Encouraging Results from Oxygen-18 Isotopic Probes

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Received: 16 June 2008 / Accepted: 7 January 2009 / Published online: 4 March 2009
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Abstract Using oxygen-18 labeled probes, the deactivation of the catalyst methyltrioxorhenium in oxidation reactions using hydrogen peroxide has been shown to result from the nucleophilic attack of HOO^- on the parent catalyst rather than by HO^- attack on intermediate **A**, opening possible routes to enhanced catalyst durability.

Keywords Methyltrioxorhenium · Olefin epoxidation · Catalyst oxidation · Isotopic labels · Peroxide adducts · Catalyst deactivation

1 Introduction

Since its discovery in 1979 [1], methyltrioxorhenium (MTO) has been recognized as among the most potent and versatile oxidation catalysts and has been broadly studied, becoming one of the better known organometallic compounds. Its potential applications in catalytic oxidations include oxidation of alkenes, conjugated dienes, alkynes, allylic alcohols, aromatic compounds, sulfur compounds, phosphines, arsines, stibines, anilines, amines and related reactions [2–22]. In most cases, green hydrogen peroxide can be used as the oxidant, and importantly, the reactions can be performed under gentle conditions with fast reaction rates, and high conversion and selectivity. Such versatile

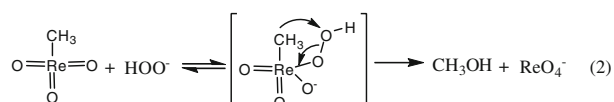
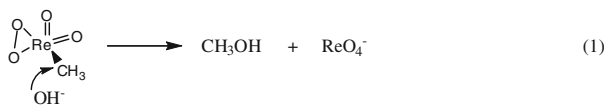
applications and facile performances have been summarized in several reviews [23–30]. However, MTO has yet to be exploited industrially, presumably because of the high cost of rhenium combined with the well known limited stabilities of organometallic compounds in the presence of oxidants. The anticipated limited in-service catalyst lifetime and challenging catalyst regeneration process may well have been factors. Recent publications by Herrmann et al. [31, 32] provided alternative synthesis and recycle processes for MTO, indicating substantial improvements in both the economics and safety of the use of the rhenium catalysts. Substantial advantages involve reduced cost and procedures involving trimethyl aluminum instead of highly toxic tetramethyl tin. However, the matter of MTO catalyst productivity remains an open issue. The results summarized here provide the means to prolong the in-service catalyst lifetime of MTO, offering a promising solution to the most serious challenge to commercial applications of MTO.

With the excellent research from Hermann [33, 34], Espenson [35, 36], Sharpless [37, 38] and others, the kinetics and mechanism of the oxidation processes catalyzed by MTO have been disclosed in much detail. Under oxidative conditions using H_2O_2 , the catalyst mainly exists in three stoichiometric forms: the parent MTO molecule and the 1:1 and 2:1 H_2O_2 :MTO adducts, known as intermediates **A** and **B** in the corresponding literature [34, 39]. In the presence of excess oxidant, the intermediate **B**, $\text{MTO} \cdot 2\text{H}_2\text{O}_2$, is stable for long periods of time, very slowly disproportionating the oxidant, H_2O_2 , into O_2 and water and simultaneously regenerating MTO. On the basis of current knowledge, the main concern for the stability of the catalyst system exists because the catalytic process of oxygen transfer to the substrate transforms intermediate **B** into intermediate **A**, the 1:1 H_2O_2 adduct, and because of the suspected instability of **A**. The destruction of the MTO

Electronic supplementary material The online version of this article (doi:10.1007/s10562-009-9855-8) contains supplementary material, which is available to authorized users.

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catalyst converts MTO, CH_3ReO_3 , into the perrhenate anion, ReO_4^- , and methanol. Mechanistic studies have shown that this process occurs by one of two pathways that are kinetically indistinguishable (Eqs. 1 and 2), both of which produce methanol as the second decomposition product. Other pathways for destruction of MTO have been eliminated by the previous studies [39].



The attempt of Espenson [39] and coworkers to complete their impressive studies of MTO mechanisms by distinguishing between the two possible decomposition pathways (Eqs. 1 and 2) using an oxygen-18 isotopic probe were limited by instrumentation to monitoring the oxygen bound to one decomposition product, perrhenate. Unfortunately, rapid oxygen exchange between the ReO_4^- and water led to inconclusive results. A more recent report [40] combined experimental and theoretical preliminary studies of MTO decomposition under the action of a variety of oxidants including H_2O_2 , IO_4^- , and PhIO . In keeping with the goals of that study, labeling experiments using periodate as the oxidant and $^{18}\text{OH}_2$ as the labeling source demonstrated the fact that the oxygen atom going to the methyl group did not originate on the MTO. However, that study did not distinguish between OH^- and HO_2^- as the likely nucleophile because of deliberate equilibration of the oxygen isotopes between the solvent and the periodate. Clearly, the formation of $\text{CH}_3^{18}\text{OH}$ might have resulted from simple nucleophilic attack of hydroxide ion on the methyl group.

2 Experimental Procedures

Potassium bicarbonate, methylrhenium trioxide, urea hydrogen peroxide and solvents were purchased from Aldrich, oxygen-18 labeled water and hydrogen peroxide were purchased from ICON.

2.1 Reaction in Normal Aqueous Solution

In a typical reaction, urea hydrogen peroxide (5 mg) was added to 0.6 mL of 0.1 M KHCO_3 (6 mg) buffered aqueous solution containing 0.1 M MTO catalyst (15 mg) to initiate the reaction at room temperature. The original

bright yellow color of MTO turned colorless immediately after adding the oxidant. The resulting reaction mixture was analyzed by GC-MS in minutes and the generated mass peaks were compared with the mass peaks of the standard methanol sample to identify the methanol peaks in the product.

2.2 Reaction in 18-Oxygen Labeled Water Solution

In a typical reaction, urea hydrogen peroxide (5 mg) was added to 0.6 mL of 0.1 M KHCO_3 (6 mg) buffered oxygen-18 water (H_2^{18}O) solution containing 0.1 M MTO catalyst (15 mg) to initiate the reaction at room temperature, and the original bright yellow color of MTO turned colorless immediately. The resulting reaction mixture was analyzed within minutes and the products were identified by GC-MS. The mass peaks of the methanol product were identical to those from procedure Sect. 2.1 and the standard methanol sample, indicating that no Oxygen-18 from solvent water was incorporated into the product.

2.3 Reaction Using Oxygen-18 Labeled Hydrogen Peroxide

In a typical reaction, 0.16 mL of 2% $\text{H}_2^{18}\text{O}_2$ (90% atom enrichment) was added to 0.6 mL of 0.1 M KHCO_3 (6 mg) buffered aqueous solution containing 0.1 M MTO catalyst (15 mg) to initiate the reaction, and immediately the original bright yellow color of MTO turned colorless as above. The resulting reaction mixture was analyzed in minutes and the product was identified by GC-MS; the observed mass peaks were compared with the mass peaks of the standard methanol sample to confirm the methanol product. The main methanol mass peaks were shifted 2 ms units from $m/z = 29, 31$ and 32 to $m/z = 31, 33$ and 34 , thereby confirming the fact that oxygen-18 from hydrogen peroxide was incorporated into the methanol product.

3 Results and Discussion

Building on the outstanding work of the Espenson group, the modified oxygen-18 labeling experiments reported here provide the missing distinction between the pathways described by Eqs. 1 and 2, and, in turn, provide important insights into the reaction mechanism that impact the ultimate value of the catalyst.

The destruction of MTO produces perrhenate ion and methanol, and this new GC-MS study focuses, for the first time, on the methanol product rather than perrhenate. The data presented here, combined with the kinetic studies of Espenson, clearly show that the catalyst deactivation occurs by the attack on CH_3ReO_3 by the nucleophile HO_2^- (Eq. 2)

and not by the alternative OH^- attack on the previously formed intermediate **A**, $\text{CH}_3\text{Re}(\text{O})_2(\text{O}_2)$ (Eq. 1). This conclusion distinguishes between the two kinetically indistinguishable processes identified by Espenson and provides insights into the operating conditions under which the catalyst system is stable, a matter that is not merely of academic interest.

The experiments for destruction of the MTO catalyst were conducted in KHCO_3 buffered aqueous solution by adding aqueous H_2O_2 , or alternatively, urea hydrogen peroxide, as the H_2O_2 source, and the product analysis was carried out by GC-MS. The results are summarized in Fig. 1. Upon addition of urea hydrogen peroxide (as the H_2O_2 source) to the KHCO_3 buffered aqueous solution of MTO catalyst, the original bright yellow color of the solution changes to colorless immediately. The resulting reaction mixture was analyzed by GC-MS in minutes.

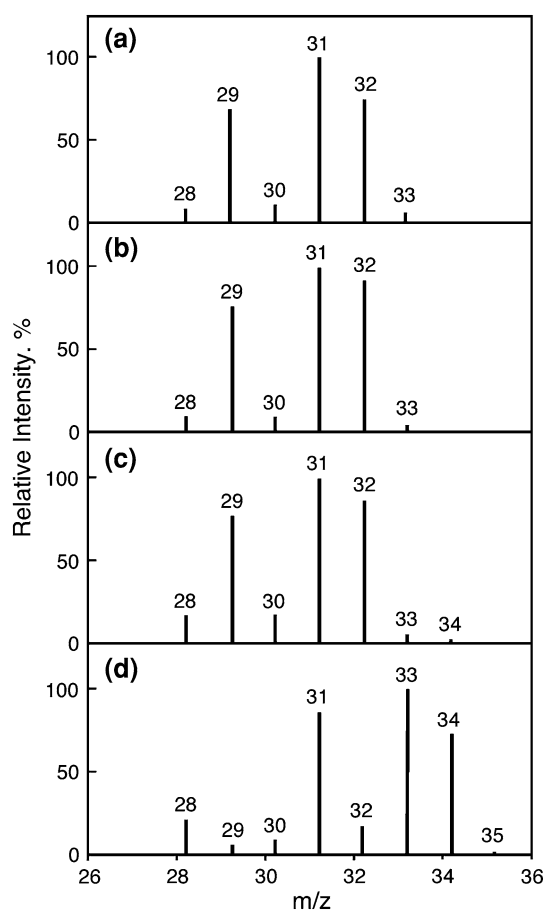
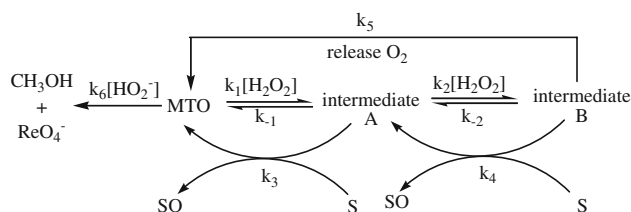


Fig. 1 The mass peaks from the GC-MS analysis for the destruction of MTO in KHCO_3 buffered aqueous solution at room temperature. **A** Standard methanol sample in aqueous solution. **B** MTO (15 mg) + KHCO_3 (6 mg) + Urea hydrogen peroxide (5 mg) in 0.6 mL H_2O . **C** MTO (15 mg) + KHCO_3 (6 mg) + Urea hydrogen peroxide (5 mg) in 0.6 mL H_2^{18}O . **D** MTO (15 mg) + KHCO_3 (6 mg) + 0.16 mL $\text{H}_2^{18}\text{O}_2$ (2% concentration with 90% atom enrichment) in 0.6 mL H_2O

Comparison with a standard spectrum identified the low molecular weight organic product as methanol (**A** and **B** in Fig. 1). Experiments using H_2^{18}O as the solvent, instead of normal water, showed no incorporation of ^{18}O in the methanol product, giving results identical to those from the standard methanol sample (**A** and **C** in Fig. 1). This provides strong evidence that the destruction of MTO does not proceed by nucleophilic attack of the OH^- anion on the methyl group of intermediate **A**; that reaction with H^{18}O^- would have produced $\text{CH}_3^{18}\text{OH}$ (Eq. 1). Further, the mass spectrum for the same reaction performed using ^{18}O labeled hydrogen peroxide (2% $\text{H}_2^{18}\text{O}_2$ aqueous solution, 90% oxygen enrichment of oxidant), displayed dominant mass peaks of methanol shifted 2 ms units from those found in the other experiments; e.g., mass peaks at $m/z = 29, 31$ and 32 were replaced by peaks at $m/z = 31, 33$ and 34 , corresponding to those of $\text{CH}_3^{18}\text{OH}$ with only minor $\text{CH}_3^{16}\text{OH}$ peaks generated by the 10% $\text{H}_2^{16}\text{O}_2$ in the ^{18}O labeled hydrogen peroxide. These data provide definitive identification of the nucleophile attacking the methyl group of MTO as H_2O_2 and not the hydroxide ion or water molecule (**D** in Fig. 1). Therefore, based on the accumulated results from oxygen-18 labeling of water and hydrogen peroxide, it is concluded that the attack of the HOO^- on the parent form of the MTO causes the catalyst deactivation (rather than the attack by the HO^- anion on the intermediate **A**).

Although the MTO catalyst demonstrates major advantages in various oxidation reactions [2–22], as mentioned above, due to its heavy catalyst cost and uncertain catalyst durability, it has not yet been exploited in industry. Understanding the catalyst deactivation mechanism, as disclosed here, may lead to the increased catalyst lifetime necessary for industrial applications.

A first qualitative assessment of enhanced catalyst durability is given here. Scheme 1 shows the forms in which the MTO catalyst exists in a functioning catalyst system and the corresponding chemical reactions. The MTO catalyst is present in three forms: the parent MTO, CH_3ReO_3 ; the 1:1 peroxide adduct, intermediate **A**, $\text{CH}_3\text{Re}(\text{O})_2(\text{O}_2)$; and the 2:1 peroxide adduct, intermediate **B**, $\text{CH}_3\text{Re}(\text{O})(\text{O}_2)_2$. The important issues are the stabilities of these three species and how those stabilities are determined by the several reactions of Scheme 1. Again, detailed studies indicate that the 2:1 H_2O_2 adduct, intermediate **B**, is sufficiently stable and only decomposes measurably with the decomposition of the peroxide, not MTO itself. The “kinetically indistinguishable pathways” of Eqs. 1 and 2 ascribe the decomposition to, respectively, the parent MTO or to the 1:1 H_2O_2 adduct named **A**. Equation 1 displays a first order dependence on H_2O_2 attributable to pre-equilibrium formation of **A** (the 1:1 adduct) that precedes the rate determining nucleophilic attack on the methyl group by OH^- . That alternative predicts that catalyst destruction would be competitive with H_2O_2



Scheme 1 The plausible oxidation process involved by the MTO catalyst

binding, following every reaction cycle, for both intermediates **A** and **B**. That would be the worst case because decomposition would be in lockstep with performing the catalytic function. In contrast, the process confirmed by these experiments and described by Eq. 2, indicates that intermediate **A** is stable. In fact, it is the process of forming **A** from MTO that is parallel to a pathway to catalyst destruction as shown in Scheme 1. It follows that minimizing the concentration of the MTO catalyst during the reaction time is a predicted route to maximizing catalyst lifetime. In turn, this suggests operating with H_2O_2 at sufficient excess to maintain intermediate **B** as the dominant catalyst species, with in-service recycle occurring between stable intermediates **A** and **B**.

In summary, using oxygen-18 isotopic probes, it has been established that the deactivation of the MTO catalyst occurs by nucleophilic HOO^- attack on the parent catalyst, MTO, resulting in formation of methanol and perrhenate ion. This finding eliminates the possibility that intermediate **A** is unstable and susceptible to hydrolytic decomposition. In turn, this provides guidance to efforts to extend catalyst durability and improve the suitability of MTO for industrial applications in industrial catalytic oxidations.

Acknowledgments Support by the National Science Foundation Engineering Research Center Grant (EEC-0310689) is deeply appreciated. We also thank R. C. Drake for his assistance on GC-MS analysis.

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