

## Oxygenation of Organotin Compounds Catalyzed by the $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ Polyoxometalate

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In recent years we have observed and formulated a unique electron transfer-oxygen transfer (ET-OT) mechanism for oxygenation of organic substrates. Thus, Keggin polyoxometalate compounds containing vanadium, most notably  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  react with organic substrates through electron transfer from the substrate to the catalyst followed by oxygen transfer from the polyoxometalate to the substrate. A reduced species vanadium(IV) species was found to be the reactive intermediate. In a complete catalytic cycle the polyoxometalate catalyst is reoxidized by  $\text{O}_2$ .

In this contribution, we will discuss stoichiometric and catalytic oxidation of organotin compounds in the presence of polyoxometalates containing vanadium. The oxygenation of tetrabutyltin to the corresponding 1-butanol and bis(tributyltin) oxide catalyzed by  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  proceeds by a electron transfer-oxygen transfer (ET-OT) mechanism. First, a  $\text{Bu}_4\text{Sn}$  reacts with  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  to yield a cation radical tetrabutyltin reduced polyoxometalate ion pair,  $[\text{Bu}_4\text{Sn}^+][\text{H}_5\text{PV}^{\text{IV}}\text{V}^{\text{V}}\text{Mo}_{10}\text{O}_{40}]$ , that was identified by NMR, mass spectrometry, and UV-visible and EPR spectroscopy. At elevated temperatures this intermediate decomposed to 1-butanol, isomeric butenes and  $(\text{Bu}_3\text{Sn})_2\text{O}$ . Experiments with 18-O labeled polyoxometalate supports the oxygen transfer from the polyoxometalate to oxidation products. Under aerobic conditions, catalytic cycles can be realized with formation of mostly 1-butanol.

Some mechanistic insight on the oxidation of *n*- $\text{Bu}_4\text{Sn}$  was obtained using density functional theory (DFT) calculations to probe the energetic and electronic basis for the observed reactivity.

The mechanistic research suggests that the phenomenon of electron transfer with subsequent oxygen transfer is the prevalent mechanism in  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  catalyzed oxygenation reactions as has also previously been shown for the oxidation of anthracene, xanthene, primary alcohols, vicinal diols and sulfides [1-3].

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[2] A. M. Khenkin, R. Neumann, *J. Am. Chem. Soc.* **2008**, *130*, 14474-14476.

[3] A. M. Khenkin, G. Leituss, R. Neumann, *J. Am. Chem. Soc.* **2010**, *132*, 11446-11448.