

The Mechanism of Olefin Oxidations
by an Oxygen-binding Cobalt Complex

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Oxidations are key steps in the industrial synthesis of most compounds made. Therefore understanding the mechanisms by which these types of reactions occur is important not only synthetically but also commercially. In many cases oxidations are catalyzed by transition metal complexes to overcome kinetic sluggishness as well as to control the number of products formed. Previous work in this group has centered on the activation of dioxygen toward oxidation of substituted phenols by binding to a cobalt Schiff-base complex.[1] In the course of this work it was found that this complex, cobalt bis(salicylidene- γ -iminopropyl)methylamine, abbreviated CoSMDPT, was also able to oxidize terminal olefins to form methyl ketones and the corresponding secondary alcohols catalytically.[2] The mechanism of this reaction was investigated.

Many homogeneous oxidations catalyzed by transition metal complexes, especially involving first row metals, proceed by autoxidation, or free radical chain pathways. When olefins are the substrates a variety of products are formed including allylic ketones, alcohols, and hydroperoxides, rather than the methyl ketones and carbinols observed for the CoSMDPT-catalyzed reaction. Experiments were conducted to rule out this most common mechanism, as well as a Wacker-type pathway [3] and the involvement of peracids in the oxidation.

Neither peracids nor superoxide ion could replace dioxygen as the oxidant in the system. However, it was found that catalytic oxidation of olefins did take place when hydrogen peroxide was used and the reaction was carried out under argon (or nitrogen), as long as CoSMDPT was also present.

The mechanism proposed for this oxidation involves formation of a cobalt hydroperoxide as the active catalyst in the system, formed either by addition of hydrogen peroxide produced *in situ* to the five-coordinate cobalt complex or by abstraction of a hydrogen atom from the solvent by the cobalt-dioxygen species. The Co-OOH is then added across the double bond of the alkene in a Markovnikoff fashion and leads to an alkyl hydroperoxide. Subsequent decomposition of the alkyl hydroperoxide by the Haber-Weiss mechanism,[4] involving both Co(II) and Co(III), yields the observed ketone and alcohol products. Deactivation of the catalyst is caused by oxidation of the bis(salicylidene- γ -iminopropyl)methylamine ligand as well as formation of a μ -peroxocobalt dimer.

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