Activation of Dioxygen

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Oxidations of organic compounds are thermodynamically favorable, yet this spin-forbidden reaction usually is kinetically sluggish. Numerous biological and industrial processes require (1) the partial oxidation of a substrate and (2) a reasonably fast reaction rate. One way to accelerate these spin-forbidden reactions may be to employ metal-dioxygen complexes ($M-O_2$) as reagents or catalysts since the dioxygen spin state and basicity changes upon coordination. Hence, dioxygen binding and activation by transition metals has been studied intensively [1] to elucidate the factors that influence metal-dioxygen bond formation and the electronic structure of the resultant adduct.

The cobalt-dioxygen complexes are of particular interest because adduct formation is reversible yet they are sufficiently stable for facile characterization and study. This unusual paramagnetic complex forms when two unpaired electrons spin-pair upon O_2 coordination. The remaining unpaired electron resides exclusively on the dioxygen ligand and indirectly spin-polarizes the cobalt d-orbitals [2].

The purpose of the investigation described herein is to demonstrate direct activation of dioxygen by a metal does occur, and to observe changes in the character of the dioxygen ligand as the ligand field strength about the metal is altered.

Van Dort reports that substituted phenols are converted catalytically to the corresponding quinones by cobalt complexes [3]. Results of kinetic and mechanistic studies support a reaction scheme [Figure 1] where cobalt-dioxygen is required in two distinct steps in the catalytic cycle. Mechanisms responsible for catalyst [Figure 2] deactivation are described briefly [4].
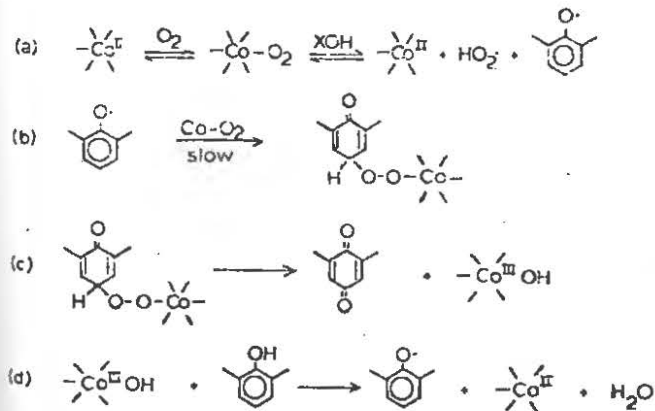
PROPOSED MECHANISM

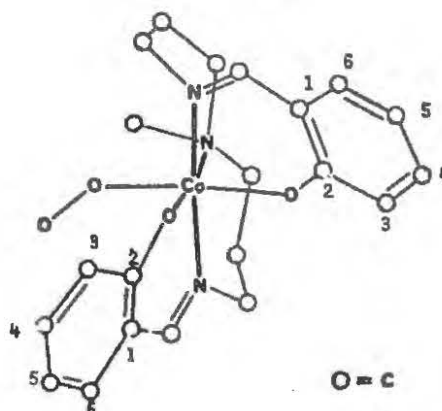Probable conformation of Co(SMDPT)

Figure 1

Figure 2

The role of ligand substituents on the reaction rate and product distribution are dramatic. Preliminary studies show that catalyst modification can (a) lead to steric blocking of the active site or (b) alter the basicity of the dioxygen ligand. Finally, the catalyst attacks carbon-carbon double bonds. Several reactions of this type are discussed [for example, Figure 3] [5]. Evidence is presented to support the direct attack of a metal activated dioxygen on the double bond.
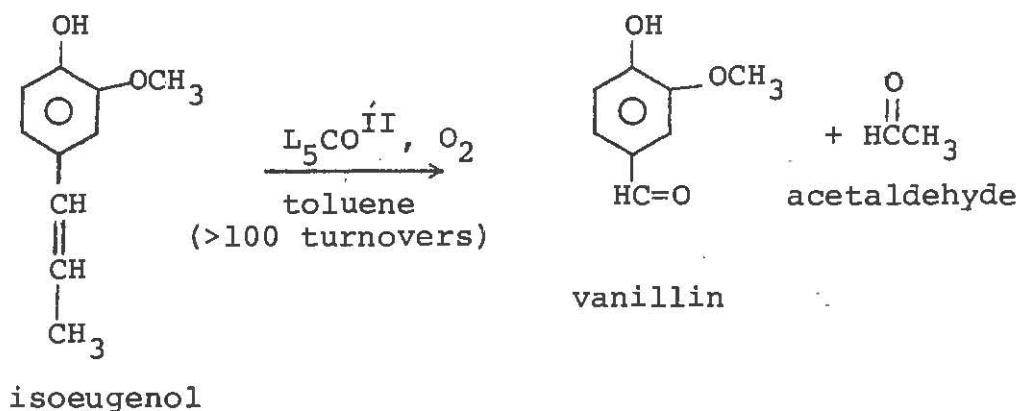

Figure 3

References

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   Structure in figure 2 is based on μ-oxo dimer, see Lindblom, Schaefer, and Marsh, Acta. Crystallogr., B, 1971, 27, 1461.

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