

C-O Bond Activation Of Organic Substrates By Transition Metal Complexes

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Many important industrial processes involve C-O bond formation, including the synthesis of acetone from propylene over a mixed $\text{SnO}_2\text{-MoO}_3$ metal surface [1,2] and the oxidation of ethylene to ethylene oxide over a Ag-based catalyst [3]. As opposed to the numerous C-O bond making processes, there are relatively few reaction classes that have been incorporated into industrial processes which involve the breaking of a C-O bond. One example is the Fischer-Tropsch process, which converts synthesis gas (CO/H_2) to a broad spectrum of compounds. These range from complex hydrocarbon mixtures to various kinds of oxygenates [4].

To gain a better understanding of the possible species which might be involved in C-O bond formation processes, many groups are currently studying the mechanism(s) of these reactions. In particular, olefin epoxidation via metal-oxo with macrocyclic ligands is under active investigation [5].

Kilty [6] and Santen [7] have independently studied the oxidation of ethylene over a Ag surface which has been preadsorbed with molecular oxygen. Both have postulated that the key to forming ethylene oxide selectively is in how the molecular oxygen is adsorbed onto the metal surface. However, neither addressed the issue of the possible intermediates or transition structures which could be involved in such a reaction. Four possible mechanisms are outlined in Scheme I. These include a direct oxygen abstraction in a concerted manner, formation of an oxametallacycle, involvement of a 1,4 biradical, or of a zwitterionic species [5,8].

From the principle of microscopic reversibility, these mechanisms are also relevant to metal mediated oxygen atom abstraction from epoxides. Several groups have engaged in studying deoxygenation of epoxides by activating the C-O bond with different transition metal complexes. In 1989, Bergman and co-workers postulated an alternate mechanism to those in Scheme I, involving initial C-H activation by the metal complex by inserting into the C-H bond of the epoxide. The metalated epoxide is then observed to undergo rearrangement to give the corresponding enolate species [9].

Moloy [10], Mayer [11], and Bercaw [8] have each independently investigated the mechanism of deoxygenation reactions. Mechanistic data presented by both Mayer and Bercaw groups have provided convincing evidence that their systems probably do not proceed through any long-lived intermediates such as oxametallacycles, but rather they involve concerted reactions. These observations are in accord with Jorgensen's theoretical calculations [12].

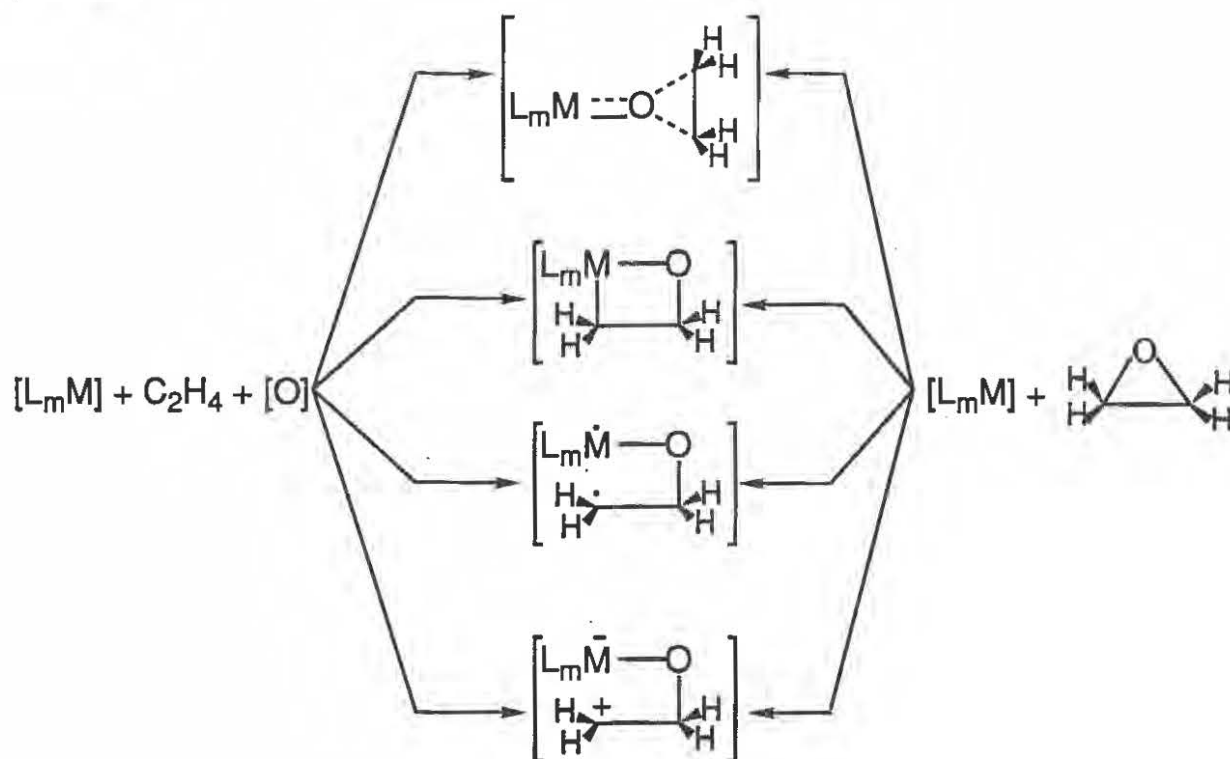
C-O bond activation in other oxygen-containing substrates have also been studied in recent years. These substrates include ketones [13-15], carbon dioxide [16-18], and esters [19-21].

The reaction of $\text{WCl}_2(\text{PMePh}_2)_4$ with ketones is remarkable in several respects. First, relatively strong C-O double bond (~ 150 kcal/mole) is simply cleaved to two divalent fragments which remain coordinated to the same metal center. Second, this is formally a four electron oxidative addition reaction which occurs under mild conditions. Third, the reaction contrasts with typical reduction of ketones by metals, which leads to pinacolates and olefins via C-C coupling. Finally, this process is loosely analogous to the reverse of an ozonolysis of an alkene.

Reactions of esters by Yamamoto [19-20] and Ito [21] have shown that the scission of the carboxylic ester bond is dependent on the nature of the ester. Two types of cleavage, α - or β -cleavage relative to the carbonyl unit, are possible.

In conclusion, the results and mechanistic insights presented here regarding the deoxygenation of oxygen-containing substrates should form the basis for a better understanding of the mechanism(s) for C-O bond forming processes.

Scheme I



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