Metal Catalyzed Olefin Epoxidation Using Hydroperoxides

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Introduction

The use of complexes of Group IVB, VB and VIB metals as catalysts in the epoxidation of olefins using organic hydroperoxides has achieved wide industrial application. The report by Indictor and Brill [1] in 1965 of the epoxidation of olefins using catalytic amounts of soluble Mo, V, and Cr complexes and *tert*-butyl hydroperoxide precipitated much of the industrial application. Today the Halcon process as a source of propylene oxide generates over three million tons of product and a billion dollars in sales a year.

A myriad of complexes [3,4] can catalyze these epoxidations, but complexes of molybdenum such as $Mo(CO)_6$ and $MoO_2(acac)_2$ have the widest application because of their high selectivity and reactivity [5]. The complexes of V(V) such as $VO(acac)_2$ also are of particular interest because of their unusual selectivity for the epoxidation of allylic alcohols [6].

Mechanistic Aspects

Sheldon in 1974 isolated the same Mo(VI) complex from both the $Mo(CO)_6$ and $MoO_2(acac)_2$ catalyzed reaction mixtures. He postulated that Mo(VI) and the respective highest oxidation states of V, W, Ti and Cr were the true catalytic species due to oxidation by hydroperoxide, and that these probably contain an oxometal functional group. He then rationalized the relative activities of the various metal complexes on the basis of how good a Lewis acid their respective metal oxides are.

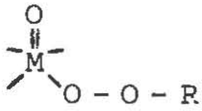
$$CrO_3,\ MoO_3 \gg WO_3 > TiO_2,\ V_2O_5$$

Mimoun [7] in 1970 reported the synthesis of $Mo(O_2)_2OL_2$ by reacting MoO_3, ligand (L), and H_2O_2. This complex was found to selectively epoxidize 2 equivalents of olefin, and he proposed it as a possible intermediate in the organic hydroperoxide epoxidations. The general rate law for the reaction is shown in equation (1) which led Mimoun

$$-\frac{d[Mo(O_2)_2OL_2]}{dt} = \frac{a[Mo(O_2)_2OL_2][Olefin]}{b + c[Olefin]} \tag{1}$$

to conclude that the olefin is involved in competition with the ligand for a coordination site on the molybdenum. He also proposed the formation of a 5-member 1,3-dipolar cyclic intermediate in the formation of the epoxide. Arakawa and Ozaki [8] were able to isolate an analogous $Mo(O_2)_2O$ complex from a reaction mixture composed of MoO_3, *t*-BuOOH, and HMPA in dichloroethane by quenching the reaction mixture with bipyridine. Sharpless, *et al*. [9], were unable to isolate any such intermediate from an analogous benzene solution; however, they did not use bipyridine as a quenching agent. Sharpless [10] reported ^{18}O labeling studies and the relative rates of norbornene:cyclohexene for $Mo(O_2)_2OL_2$ and several systems with known cyclic transition state sizes, the results of which he contends are more consistent with a three-center transition state rather than the 5-member transition state proposed by Mimoun.

Sharpless, *et al.* [9], reported an ^{18}O study of the reaction of *tert*-butyl hydroperoxide of two different olefins catalyzed by $MoO_2(acac)_2$ and $VO(acac)_2$. These labeling studies were inconsistent with a $Mo(O_2)_2O$ type intermediate. They proposed an alternative intact hydroperoxide with coordination most likely occurring through the hydroxy oxygen (Structure I). The specificity of V(V) for allylic alcohols was explained by the formation of a vanadate ester intermediate (Structure II). Sheldon [11] has explained the isolation of the $Mo(O_2)_2O$ species by Arakawa and Ozaki by a pH dependence of the catalytic species, with the bis-peroxo species being observed in significant concentration only in basic solutions. Mimoun [12] has proposed a new catalytic cycle incorporating the intact coordinated hydroperoxide but maintaining olefin coordination and the 5-member cyclic intermediate.



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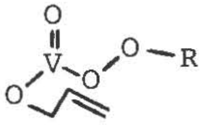

II

Applications

Milhelich, *et al.* [13,14], have used the Sharpless model of a vanadate ester intermediate and simple steric considerations to predict product selectivities for various acyclic homoallylic alcohols. Sharpless and coworkers [15,16] have been able to generate assymetric epoxidations of olefinic alcohols in extremely high optical purity using titanium tartrate complexes and *t*-BuOOH.

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