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Oxidation of Styrene

The oxidation of styrene, catalysed by the vanadium complexes, was carried out in acetonitrile using 30% aqueous H_2O_2 as oxidant to give benzaldehyde (bza), 1-phenylethane-1,2-diol (phed), benzoic acid (bzac), and phenylacetaldehyde (phaa). Reaction conditions were optimised considering 7 as a representative catalyst and varying the reaction parameters to achieve maximum oxidation of styrene.

Three different amounts viz. 0.1, 0.2, and 0.3 mmol of 7 were taken at the fixed amount of styrene (5 mmol), aqueous 30% H_2O_2 (10 mmol) in $C[H_3]CN$ (10 ml), and the reaction was carried out at 80[degrees]C. The obtained conversions (amount of styrene reacted) were plotted as a function of time. The reaction conditions were also optimised varying the temperature (50-80[degrees]C), and the amount of H_2O_2 (5, 10, and 15 mmol). The conversion increased with temperature, and at 80[degrees]C the use of 10 mmol of aqueous 30% H_2O_2, CH_3CN (10 ml) and 0.1 mmol of catalyst were found optimum for the conversion of 5 mmol of substrate. Therefore, these reaction conditions were selected to carry out further catalytic studies.

Catalytic activities of other complexes vary within this range. Overall, V complexes with reduced ligands (V-pyran) perform better than with nonreduced ligands (V-pyren), and catalysts involving diaminocyclohexane-containing ligands are more active than those derived from diphenylethylenediamine. The most commercially interesting product, styrene oxide, is not found in the reaction products, probably because after its formation it was transformed into other products. The selectivity of benzaldehyde is the highest (>85%), and this is possibly due to nucleophilic attack of [H.sub.2][O.sub.2] to styrene oxide, formed during the reaction, followed by cleavage of the hydroperoxystyrene intermediate. Benzaldehyde formation may also be facilitated by direct oxidative cleavage of the styrene side-chain double bond via a radical mechanism.

The formation of benzoic acid through benzaldehyde is quite likely. Isomerization of styrene oxide may yield phenyl acetaldehyde. Hydrolysis of styrene oxide to some extent by water present in [H.sub.2][O.sub.2] to 1-phenylethane-1,2-diol is also a plausible pathway for the formation of this product.

Oxidation of Cyclohexene

Under similar reaction conditions as those used for the oxidation of styrene, we have also carried out the oxidation of cyclohexene. Again, a very similar trend was obtained, i.e., highest conversion (71%) with complex 7 and lowest (41%) with 6. Once again within the ligand system, the complexes with the pyran-type ligands have shown better performance than the complexes with the pyren-type ligands, but the most relevant difference is found in the type of diamine backbone, with the cyclohexanediamine derivatives showing conversions higher than 71%, and the diphenyldiamine derivatives lower than 47%.

The selectivity of the reaction products follows the order: cyclohexane-1,2-diol > cyclohex-2-enol > cyclohex-2-enone [approximately equal to] 1,2-epoxycyclohexane. Thus, with a selectivity >70%, cyclohexane-1,2-diol is the most important product and is probably the result of the oxidation of 1,2-epoxycyclohexane. A range of 11-18% selectivity is found for the second highest product, cyclohex-2-enol. Epoxycyclohexane results from the oxidation of the double bond, while the allylic-oxidation pathway, forming cyclohex-2-enone and cyclohex-2-enol, reflects the preferential attack of the activated C-H bond over the C=C bond.

Oxidation of Cumene

The oxidation of cumene gave acetophenone, 2-phenylpropanal, 1,2-epoxy-2-phenylpropane, and 2-phenylpropan-2-ol; Scheme 4. After several trials using 0.1 mmol of catalyst, the optimised reaction conditions for the maximum oxidation of 3 mmol of cumene were found to be aqueous 30% H_2O_2 (9 mmol), acetonitrile (10 ml) at 80[degrees]C, and the results reported were carried out under these conditions.