Oxidation of Hydrocarbons with Hydrogen Peroxide Catalyzed by Zinc Containing Polyoxometalate

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Zinc heteropolyanion, $PZnMo_2W_9O_{39}{}^{5-}$, was found to be an efficient catalyst for alkene epoxidation and oxidation of alkylaromatic compounds with 30% H_2O_2. Epoxide selectivities in the range of 80 to 100% was observed.

Numerous hydrocarbon oxidation systems based on metalloporphyrin derivatives that mimic the activity of cytochrome P-450 have been reported.[1] However degradation of the common synthetic metalloporphyrins in the presence of strong oxidizing agents has prevented their practical applications. Heteropolyoxometalates as oxidatively stable inorganic porphyrins have received much attention as homogeneous catalysts because of their ability to utilize environmentally and economically acceptable hydrogen peroxide as oxygen donor.[2,3] Catalytic oxidation with hydrogen peroxide has been limited to polyoxometalates containing only electron-poor metals in d^0 state,[4-7] or disubstituted polyoxometalates with general formula $[WM_2(ZnW_9O_{39})_2]^{12-}$, where M are Mn^{2+}, Pd^{2+} or Pt^{2+}.[8,9]

We now report the use of an oxidatively stable zinc-substituted polyoxometalate, $[(n\text{-}C_4H_9)_4N]_5PZnMo_2W_9O_{39}$, as catalyst for the epoxidation of alkenes and hydroxylation of alkylaromatics with promising selectivity. The tetra-*n*-butyl ammonium salts of the transition metal substituted heteropolytungstate complexes $[P(M^{n+})Mo_2W_9O_{39}]$ ($M = Fe^{3+}$, Mn^{2+}, Zn^{2+}, Co^{2+}) were prepared from $\alpha\text{-}K_7PMo_2W_9O_{39}$[10] by a slight modification of the previously reported method.[11] The formation of Keggin structure and composition of the compounds were confirmed by IR, ^{31}P NMR and elemental analysis.[12] Thermal gravimetric analysis was performed on all of the compounds (between 40 and 240 °C). The results indicated that the hydration numbers are between 3 to 6.

A typical reaction was run as follows : 1 mmole substrate and 0.05 mmole $[(n\text{-}C_4H_9)_4N]_5PZnMo_2W_9O_{39}$ in 10 mL chloroform were introduced into a 50 mL flask equipped with a magnetic stirrer. The mixture was heated to 60 °C and 10 mmole of 30% H_2O_2 was added. The progress of reaction was monitored by GLC. The reaction products were extracted with CH_2Cl_2 (20 mL) and purified by a silica gel plate or silica gel column. The identities of products were confirmed by IR and ^1H NMR spectral data.

Table 1. Epoxidation of cyclooctene with 30% H_2O_2 by various polyoxometalates[a]

Run	Catalyst	Epoxide Yield (%)[b]
1	$[(n\text{-}C_4H_9)_4N]_5PCoMo_2W_9O_{39}.5H_2O$	2.5
2	$[(n\text{-}C_4H_9)_4N]_5PMnMo_2W_9O_{39}.6H_2O$	13.5
3	$[(n\text{-}C_4H_9)_4N]_4PFeMo_2W_9O_{39}.5H_2O$	16
4	$[(n\text{-}C_4H_9)_4N]_5PZnMo_2W_9O_{39}.3H_2O$	90
5	$\alpha\text{-}K_7PMo_2W_9O_{39}$	2

[a]Reaction conditions: cyclooctene (1 mmole), H_2O_2 (10 mmole), polyoxometalates (0.05 mmole), chloroform (10 mL), time 4h.
[b]GLC yields based on the starting cyclooctene.

Table 1 shows results for the epoxidation of cyclooctene with H_2O_2 by various mixed addenda heteropolyoxometalates , $[(n\text{-}C_4H_9)_4N]_{7-n}P(M^{n+})Mo_2W_9O_{39}.xH_2O$ ($M^{n+} = Co^{2+}$, Mn^{2+}, Fe^{3+}, Zn^{2+}). Among these compound, Zinc-substituted polyoxometalate was found the most active catalyst.

The effect of different organic solvents on epoxidation of cyclooctene with H_2O_2 by $[(n\text{-}C_4H_9)_4N]_5PZnMo_2W_9O_{39}$ was also studied. It was observed that chloroform is the preferred solvent giving the highest conversion. Acetonitrile can be used as a possible alternative solvent.

The H_2O_2 / $PZnMo_2W_9O_{39}{}^{5-}$ epoxidizing system converts different alkenes efficiently to their corresponding epoxides (Table 2). Epoxide selectivities are ranging from 80 to 100%. With this catalytic system, (+)-limonene was mainly epoxidized to 1,2-epoxide as a mixture of *cis* and *trans* isomers after 3 hours. At longer times double epoxidation was observed.

Alkylaromatic compounds can be oxidized effectively at benzylic carbon with hydrogen peroxide as oxygen donor in a single phase homogeneous reaction using $[(n\text{-}C_4H_9)_4N]_5PZnMo_2W_9O_{39}$ as catalyst (Table 2). Ketone / alcohol ratio are ranging from 0.57 to 1.

Table 2. Oxidation of various substrates with 30% H_2O_2 catalyzed by $[(n\text{-}C_4H_9)_4N]_5PZnMo_2W_9O_{39}.3H_2O$[a]

Run	Substrate	Products	Yield (%)[b]	Time (h)
1	Cyclooctene	Cyclooctene oxide	90	4
2	Cyclohexene	Cyclohexene oxide	85	4
		Cyclohexen-2-ol	15	
3	Styrene	Styrene oxide	54	24
		Acetophenone	13	
4	α -Methyl - styrene	α -Methylstyrene oxide	83	24
5	1-Octene	1-Octene oxide	24	24
6	(+)-Camphene	(+)-Camphene oxide	36	24
7	R-(+)-Limonene	1,2-Limonene oxide	80	3
8	Ethylbenzene	Acetophenone	38	24
9	Fluorene	9-Fluorenone	12	24
		9-Hydroxyfluorene	21	
10	Diphenylmethane	Benzophenone	26	24
11	Propylbenzene	Propiophenone	15	8
12	Tetrahydro-naphtalene	α -Tetralol	27	24
		α -Tetralone	9	

[a]Reaction conditions: substrate (1 mmole), H_2O_2 (10 mmole), $[(n\text{-}C_4H_9)_4N]_5PZnMo_2W_9O_{39}$ (0.05 mmole), chloroform (10 mL).
[b]GLC yield based on the starting substrates.

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References and Notes

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12 Analytical data for the most active catalyst, $[(n\text{-}C_4H_9)_4N]_5PZnMo_2W_9O_{39}.3H_2O$, are: Elemental analysis; calculated (found): C, 25.06 (26.09); H, 4.86 (5.10); N, 1.83 (1.75); P, 0.81 (0.92); Mo, 5.01 (4.88); W, 43.20 (44.52); Zn, 1.71 (1.85); ^{31}P NMR (in CH_3CN): -10.4 ppm; IR (KBr) : 2926, 2854, 1487, 1065, 945, 890, 805, 710 cm^{-1}.