Efficient and Selective Epoxidation of Alkenes with Sodium Periodate Using Supported Manganese Porphyrins under Ultrasonic Irradiation

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Epoxides are readily obtained in high yields and good selectivities by ultrasonic irradiation of alkenes and sodium periodate in the presence of catalytic amounts of manganese porphyrins supported on polyvinylpyridine and IRA-900 ion-exchange resin.

Synthetic metalloporphyrins, like cytochrome P-450, act as useful catalysts for a variety of redox reactions.[1-3] The high efficiency of some of these catalytic systems makes them potentially useful for large scale oxidations. Immobilization of expensive metalloporphyrin catalysts on insoluble organic and inorganic supports appear to be a good way to render them practicable and improve their stability and selectivity.[4-9] However, the activity of such heterogeneous catalysts is often less than that of soluble ones, due to either chemical or diffusional restrictions. The successful applications of ultrasonic irradiation in a number of heterogeneous reactions,[10,11] prompted us to investigate the effect of ultrasonic irradiation on oxygenation reactions catalyzed by supported metalloporphyrin catalysts which are usully easy to handle but less reactive.

In this communication, we report a significant improvement in efficiency of supported metalloporphyrin catalysts through the use of ultrasonic irradiation. Higher catalytic activity was observed compared to the previously described homogeneous manganese porphyrin-periodate catalytic systems.[12,13]

Using cyclooctene as the typical alkene substrate, the two catalysts i.e. sulfonated manganese(III) tetraphenylporphyrin supported on Amberlite IRA-900 ion exchange resin (MnTPPS-Ad)[14] and sulfonated manganese(III) tetraphenylporphyrin supported on poly(4-vinylpyridine) (MnTPPS-PVP)[15] were examined under various reaction conditions. The results are summarized in Table 1. We found that sonication has general applicability for supported metalloporphyrin catalysts with different oxygen donors. Higher activity and stability of the supported catalysts was observed with sodium periodate compared to other oxygen donors under ultrasonic irradiation.

The effect of different common organic solvents such as CH_3CN, $(CH_3)_2CO$, CH_3OH, CH_3CN/H_2O and $(CH_3)_2CO/H_2O$ on epoxidation of cyclooctene with sodium periodate by supported manganese porphyrins was also studied. The same rate enhancement was obtained in all of these solvents under ultrasound irradiation. Among these solvents, CH_3CN/H_2O (1/1) mixture, which showed higher epoxide yield, was chosed as the reaction medium.

As shown in Table 2, sonication of a mixture of supported manganese porphyrins, alkene and $NaIO_4$ converts different alkenes efficiently to the corresponding epoxides.[16] Typically, 1 mmole alkene, 2 mmole $NaIO_4$, 0.2 mmole imidazole, 0.0147 mmole supported manganese porphyrin in 20 mL CH_3CN/H_2O (1/1) were sonicated in an ultrasound cleaner (40 KHz) at room temperature. Reactions were monitored by GLC and the identity of pure epoxides confirmed by ^1H NMR and MS spectral data.

Table 1. Catalytic epoxidation of cyclooctene by supported manganese porphyrins with different oxygen donors[a]

Run	Catalyst	Oxygen donor	Time/min	Epoxide / %[b]	
				U[c]	S[c]
1	MnTPPS-PVP[d]	$KHSO_5$	30	93	50
2	MnTPPS-Ad[d]	$KHSO_5$	30	100	56
3	MnTPPS-PVP[d]	NaOCl	60	82	43
4	MnTPPS-Ad[d]	NaOCl	60	94	52
5	MnTPPS-PVP	$NaIO_4$	60	100	35
6	MnTPPS-Ad	$NaIO_4$	60	95	34

[a] Reaction conditions: cyclooctene (1 mmole), oxygen donor (2 mmole), imidazole (0.2 mmole), catalyst (mass equiv. to 0.0147 mmole Mn), CH_3CN / H_2O (10 mL/10 mL). [b] GLC yield based on starting cyclooctene. [c] U: ultrasonic irradiation (40 KHz), S: stirred magnetically (1200 rpm). [d] Instead of 10 mL H_2O, 10 mL of phosphate buffer at pH=7 was added.

Table 2. Epoxidation of alkenes with periodate using supported manganese porphyrins[a]

Run	Alkene	Catalyst	Conversion/%[b]		Epoxide / %[b]	
			U[c]	S[c]	U[c]	S[c]
1	Cyclohexene	MnTPPS-Ad	92	40	88	30
2	Cyclohexene	MnTPPS-PVP	100	42	96	34
3	Styrene	MnTPPS-Ad	90	35	89	28
4	Styrene	MnTPPS-PVP	100	40	94	30
5	α-Methylstyrene	MnTPPS-Ad	100	45	92	38
6	α-Methylstyrene	MnTPPS-PVP	100	48	94	39
7	(+)-Camphene	MnTPPS-Ad	74	30	74	25
8	(+)-Camphene	MnTPPS-PVP	97	40	97	37
9	R-(+)-Limonene	MnTPPS-Ad	62	26	42[d] 20[e]	15[d] 11[e]
10	R-(+)-Limonene	MnTPPS-PVP	84	34	57[d] 27[e]	24[d] 10[e]
11	*trans*-Stilbene	MnTPPS-Ad	44	16	44[f]	16[f]
12	*trans*-Stilbene	MnTPPS-PVP	50	18	50[f]	18[f]
13	*cis*-Stilbene	MnTPPS-Ad	76	32	72[g] 4[f]	30[g] 2[f]
14	*cis*-Stilbene	MnTPPS-PVP	80	33	76[g] 4[f]	30[g] 3[f]

[a] Reaction conditions: alkene (1 mmole), $NaIO_4$ (2 mmole), imidazole (0.2 mmole), catalyst (mass equiv. to 0.0147 mmole Mn), CH_3CN/H_2O (10 mL /10 mL), time (1 h). [b] GLC yield based on starting alkene. [c] U: Ultrasonic irradiation (40 KHz), S: Stirred magnetically (1200 rpm). [d] 1,2-Epoxide; [e] 8,9-Epoxide; [f] *trans*-Epoxide; [g] *cis*-Epoxide.

To assess long-term stability for MnTPPS-PVP and MnTPPS-Ad catalysts under ultrasonic irradiation, recycling experiments were carried out with a single sample of each catalyst. Each of the catalysts were used repeatedly over styrene reactions, with the catalysts being removed by filtration at the end of each reaction, washed with water and acetonitrile and reused. The yields and leaching data obtained are listed in Table 3.

Table 3. Recycling data for supported manganese porphyrin catalysts in the epoxidation of styrene under ultrasonic irradiation[a]

Run	Conversion / %[b]	Epoxide / %[b]	Mn leached %[c]
1	100(90)[d]	94(89)	2.2(2.5)
2	95(88)	89(87)	2.1(2.3)
3	91(85)	86(82)	1.2(1.3)
4	88(83)	82(80)	1.2(1.2)

[a] Reaction Conditions: identical with those in Table 2, footnote a. [b] GLC yield based on starting styrene. [c] Reaction solutions assayed for leached Mn using atomic absorption specroscopy and expressed as percentage of Mn originally present on resin. [d] The values in paranthesis are for MnTPPS-Ad / $NaIO_4$ and other values are for MnTPPS-PVP / $NaIO_4$ systems.

Alkene oxidations catalyzed by supported manganese porphyrins under ultrasound have two main advantages over those carried out under agitation with magnetic stirrer. The first is that oxidations are faster, typically complete within 1 h compared to at least 4 h required for agitation. Secondly, generaly observed side reactions such as double bond cleavage and allylic oxidation are minimized. Further work concerning the extension of this reaction to various metalloporphyrin catalytic systems is currently under way.

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16 In most epoxidation reactions under sonication or simple stirring the MnTPPS-PVP showed higher activity than MnTPPS-Ad catalyst. This suggests that the poly(vinylpyridine) resin support leads to a better activity for the catalyst compared to the simple cationic resin (Amberlite). The reason for this behavior is proximal effect due to coordination of a pyridine unit arising from the polymer.