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Manganese Porphyrin Catalyzed Homogeneous Aqueous Oxidation of Organic Molecules by Magnesium Monoperoxyphthalate (MMPP)

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Summary: Magnesium monoperoxyphthalate (MMPP) oxidizes a variety of organic molecules in neutral homogeneous aqueous solutions at room temperature. A water-soluble porphyrin complex, *meso*-tetrakis(4-N-methylpyridyl)porphyrinatomanganese(III) chloride, Mn(III)TMPyP(4) Cl, acts as an efficient catalyst for the epoxidation and hydroxylation of water-soluble hydrocarbons.

Magnesium monoperoxyphthalate (MMPP) is a recently discovered, stable water-soluble peracid derivative.[1,2] It has been used for epoxidation,[3] Baeyer-Villiger oxidation,[3a,4] sulfur[3a,5] and nitrogen oxidation,[3a,6] and oxidative regeneration of ketones from hydrazones,[7] but no study has appeared describing the oxidation of water-soluble organic substrates by MMPP in neutral aqueous solutions. MMPP has also been found to be an efficient single oxygen atom donor in metal porphyrin-catalyzed epoxidation,[8] hydroxylation,[9] and other reactions.[10, 11] Again little is known about such catalytic reactions in neutral homogeneous aqueous solutions using water-soluble catalysts and substrates. As part of our study on semisynthetic catalytic metalloantibodies,[12] we evaluated MMPP as oxidant in such reactions at room temperature under neutral pH conditions.

The oxidations were done in NMR tubes, and conversions of reactants to products were monitored by ^1H NMR spectroscopy. Products were identified by comparing their ^1H and ^{13}C NMR spectra with those of authentic samples. A typical experimental procedure involves preparing a known concentration of a substrate in Na_2DPO_4/KD_2PO_4 buffered D_2O solution and recording the NMR spectrum. MMPP was then introduced and the spectra were recorded after appropriate time intervals. It should be noted that no optimization of the reaction conditions such as pH, temperature, and ionic strength was undertaken. Moreover slow decomposition of the oxidant occurs in the absence of the substrate.

The results of uncatalyzed oxidations at room temperature at neutral pH in Table 1 show that MMPP is an efficient oxidant for the aqueous oxidation of alkenes, aldehydes, thiols, sulfides, and pyridine, but it does not hydroxylate $4\text{-}^iPrC_6H_4SO_3Na$ or oxidize ketones and alcohols. The conversions for alkenes vary (50-85%) depending on their reactivity and therefore their efficiencies in competing with the decomposition of the oxidant, but the yields of the epoxide are uniformly very high. From the order of reactivity of different alkenes it appears that MMPP is an electrophilic epoxidizing agent as previously observed.[2] Increasing the concentration of MMPP leads to more rapid epoxidation of $4\text{-}CH_2\text{=}CH\text{-}C_6H_4SO_3Na$, and increasing the initial pH from 6.5 to 7.8 slows down the reaction leading to lower conversions.

Table 1 Oxidation of water-soluble organic molecules by MMPP at neutral pH[a]

Substrate	conc. (M)	time	conv. (%)	product(s)	selectivity (%)
$CH_2=C(Me)CH_2SO_3Na$	0.15	8.5 h	58	epoxide	98[b]
$4\text{-}CH_2=CHC_6H_4SO_3Na$	0.10	1.5 h	85	epoxide	99[c]
$4\text{-}CH_2=CHC_6H_4SO_3Na$	0.11	16 h	75	epoxide	98[b]
$4\text{-}CH_2=CHC_6H_4SO_3Na$	0.11	15 h	50	epoxide	98[b,d]
trans-MeCH=CHCOOH	0.17	90 h	72	epoxide	99[b]
$CH_2=CHCH_2COOH$	0.15	18 h	65	epoxide	99[b]
$CH_2=CHCOCH_3$	0.22	18 h	65	epoxide	98[b]
$1,2,3\text{-}(HO)_3C_6H_3$	0.08	1.0 h	20	quinone	
pyridine	0.21	30 m	99	N-oxide	99
$4\text{-}Me_2CHC_6H_4SO_3Na$	0.09	22 h		no reaction	
$4\text{-}CH_3COC_6H_4SO_3Na$	0.11	72 h		no reaction	b
$2\text{-}HCOC_6H_4SO_3Na$	0.08	9 h	100	-COOH	99
$CH_3CHOHCH_3$	0.16	70 h		no reaction	b
L-cysteine	0.10	5 m	98	$-SO_3H$	100[e]
D-methionine	0.08	5 m	100	-SO-	86
D-methionine	0.11	10 m	100	$-SO_2-$	100[c]

a. All reactions run at RT using 1 equiv. MMPP at pH=6.5 unless otherwise stated. b. At the time indicated, no oxidant remained. c. 2 equiv. MMPP used. d. pH=7.8. e. 3 equiv. MMPP used.

Table 2 Oxidation of water-soluble organic molecules by MMPP at neutral pH catalyzed by Mn(III)TMPyP(4)[a,b]

Substrate	conc. (M)	time (m)	conv. (%)	product(s)	selectivity (%)
$CH_2=CH(Me)CH_2SO_3Na$	0.12	5	12	epoxide	98[c]
trans-MeCH=CHCOOH	0.12	3	5	epoxide	99[d]
$4\text{-}CH_2=CHC_6H_4SO_3Na$	0.08	2	99	epoxide	99[e]
$4\text{-}Me_2CHC_6H_4SO_3Na$	0.08	3	65	alcohol	90[f]
$4\text{-}CH_3CH_2C_6H_4SO_3Na$	0.09	2	46	alcohol	35[f]
				ketone	65

a. All reactions run at RT using 1 equiv. MMPP and with 0.5 mg of the catalyst at pH=6.5. b. The catalyst was destroyed within 20-30 sec. in all reactions, and the solutions colourless in 1 m. Addition of substrate after bleaching showed no reaction. c. Same reaction (0.15 M) without catalyst gave 2% epoxide in 10 m. d. Same reaction (0.17 M) without catalyst gave no detectable epoxide in 5 m. e. Same reaction (0.11 M) without catalyst gave 5% epoxide in 5 m. f. No reaction occurred without catalyst.

The results of oxidations catalyzed by *meso*-tetrakis(4-N-methylpyridyl)porphyrinatomanganese(III) chloride, Mn(III)TMPyP(4) Cl, are shown in Table 2. The manganese porphyrin complex efficiently catalyzes both epoxidation and hydroxylation of water-soluble hydrocarbons, but the decomposition of the catalyst under present conditions leads to high conversions only for the most reactive substrate ($4\text{-}CH_2=CHC_6H_4SO_3Na$). However, even with the other two alkene substrates in Table 2, catalysis is significant. Most noteworthy is the hydroxylation of $4\text{-}EtC_6H_4SO_3Na$ and $4\text{-}{}^iPrC_6H_4SO_3Na$, with the latter giving higher conversion in contrast with previously reported results .[9]

Finally, the catalyzed epoxidation of $4\text{-}CH_2=CHC_6H_4SO_3Na$ under various conditions was briefly examined, Table 3. Among three porphyrin complexes examined, only Mn(III)TMPyP(4) shows high activity.

With lower substrate/catalyst ratios, the stability of the catalyst is improved. While the analogous cobalt complex Co(III)TMPyP(4) Cl catalyzes the decomposition of MMPP, the anionic *meso*-tetrakis(4-sulfonatophenyl)-porphyrinatomanganese(III) (Na salt), Mn(III)TPPS(4), shows no apparent catalytic activity. This may be due to electrostatic repulsions between the SO_3^- groups of the catalyst and the substrate preventing proper orientation of the two for reaction; however, ion pairing is less likely in the polar medium of aqueous solutions than in most organic solvents. Therefore, the lack of catalysis by the Mn(III)TPPS(4) complex is probably due to the lower intrinsic reactivity in these reactions and/or increased susceptibility to oxidative decomposition of the anionic metalloporphyrin when compared to the Mn(III)TMPyP(4) complex.

Table 3 Catalyzed oxidation of 4-CH_2=$CHC_6H_4SO_3Na$ by MMPP at neutral pH[a]

conc. (M)	catalyst[b]	sub./cat. ratio	time (min.)	conv. (%)	epoxide selectivity (%)	solution color
0.11	MnTMPyp	135	2	100	99	brown[c]
0.11	MnTMPyP	138	2	100	99	light yellow
0.24	MnTMPyP	1230	10	85	99	brown
0.27	MnTMPyP	705	5	95	99	brown
0.07	MnTMPyP	58	2	95	99	deep red[d]
0.14	MnTMPyP	175	3	96	99	brown[e]
0.12	MnTPPS	650	5	0	-	colorless[f]
0.13	CoTMPyP	700	2	0	-	light red[g]

a. All reactions run at RT using 1 equiv. MMPP at pH=6.5 except the last two where initial pH=6.8. b. See text for catalysts . c. With 2.0 mg imidazole present, UV-vis showed only weak Soret band. d. UV-vis indicated catalyst to be little changed. e. At 21 h, addition of 0.1 M of substrate and MMPP re-initiated catalysis with high turnover numbers and rate to give the epoxide. f. MMPP was not decomposed. g. MMPP was completely decomposed.

In summary, we found that MMPP is an efficient oxidant in neutral homogeneous aqueous solutions at room temperature for a variety of organic molecules. In association with the cationic metal porphyrin catalyst Mn(III)TMPyP(4) Cl it is also an efficient single oxygen atom donor.

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