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Selectivity in Oxidation of Sulfides with Hydrogen Peroxide by $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3PM_{12}O_{40}{}^{3-}$ and $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3\{PO_4[M(O)(O_2)_2]_4\}^{3-}$ (M=Mo or W)

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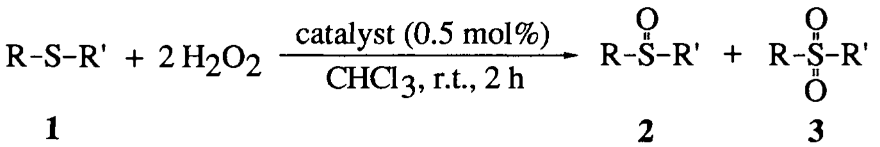
Dramatical difference in selectivity was observed in the hydrogen peroxide oxidation of sulfides by $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3PW_{12}O_{40}{}^{3-}$ (CWP) and $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ (PCWP) under the two-phase system using chloroform as the solvent. The oxidation of sulfides with 35% H_2O_2 by CWP afforded the corresponding sulfoxides in high selectivity (93-99%), while the same oxidation by PCWP gave sulfones exclusively.

Previously, we showed that treatment of $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3PMo_{12}O_{40}{}^{3-}$(CMP) with excess hydrogen peroxide gives a peroxomolybdenum compound1) which is subsequently identified to $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3\{PO_4[Mo(O)(O_2)_2]_4\}^{3-}$ (PCMP). However, by the same treatment of CWP with hydrogen peroxide no peroxotungsten compound was formed. In order to obtain the corresponding peroxotungsten complex PCWP, 12-tungstophosphoric acid (WPA) in excess 35% H_2O_2 must be allowed to react with cetylpyridinium chloride (CPC) in water.2) The crystal structure of peroxo complexes having the general formulae, $Q_3\{PO_4[W(O)(O_2)_2]_4\}$ (Q^+ = onium group), was first confirmed by Venturello *et al.*3) Recently, Brégeault *et al.* have shown the alternative preparation method for $Q_3\{PO_4[M(O)(O_2)_2]_4\}$ (M = Mo4) or W5)). Thus, it has been increasing interest in the relationship between the structure of heteropolyoxometalates and their behavior in hydrogen peroxide oxidation processes.4-7)



$$\underset{\textbf{1}}{R\text{-}S\text{-}R'} + 2\,H_2O_2 \xrightarrow[\text{CHCl}_3,\ \text{r.t., 2 h}]{\text{catalyst (0.5 mol\%)}} \underset{\textbf{2}}{R\text{-}\overset{O}{\overset{\|}{S}}\text{-}R'} + \underset{\textbf{3}}{R\text{-}\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}\text{-}R'}$$

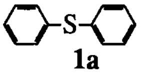
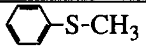
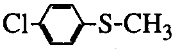
1 **2** **3**

Scheme 1.

In this paper, we wish to report more insight on the reactivity of the peroxo species generated from cetylpyridinium molybdo- and tungstophosphates and hydrogen peroxide in the catalytic cycle. The oxidation of sulfides (**1**) to sulfoxides (**2**) and sulfones (**3**) was chosen as a model reaction7,8) (Scheme 1).

Table 1 shows representative results for the oxidation of sulfides with 35% H_2O_2 by several cetylpyridinium metalophosphates. It is very interesting to compare the selectivity in the oxidation of diphenylsulfide (**1a**) by molybdophosphates and tungstophosphates. The oxidation of **1a** with 35% H_2O_2 (2 equiv.) by CMP and PCMP in chloroform at room temperature gave approximately 3:1 mixture of diphenylsulfoxide (**2a**) and diphenylsulfone (**3a**) in 61% and 70% conversions, respectively. In contrast to the above observations, a marked difference in selectivity was observed in the oxidation of **1a** between CWP and PCWP. The oxidation of **1a** catalyzed by CWP proceeded with high selectivity to give **2a** more than 99% in 64% conversion. By PCWP, however, **1a** was completely converted into **3a** without formation of **2a**. In oxidations of methylphenylsulfide (**1b**) and methyl-4-chlorophenylsulfide (**1c**) by molybdo- and tungstophosphates, the selectivities to sulfoxides, **2b** and **2c**, and sulfones, **3b** and **3c**, were similar to those observed in the oxidations of **1a** by both catalytic systems (runs 5-12).

Table 1. Hydrogen Peroxide Oxidation of Sulfides Catalyzed by Cetylpyridinium Molybdo- and Tungstophosphates[a]

Run	Sulfide	Catalyst	Conv. / %	Selectivity / %[b]	
				2	3
1	 **1a**	CMP	61	**2a** 76	**3a** 24
2	**1a**	PCMP	70	74	26
3	**1a**	CWP	64	<99	>1
4	**1a**	PCWP	100	0	100
5	 **1b**	CMP	87	**2b** 44	**3b** 56
6	**1b**	PCMP	93	32	68
7	**1b**	CWP	91	93	7
8	**1b**	PCWP	100	0	100
9	 **1c**	CMP	93	**2c** 41	**3c** 59
10	**1c**	PCMP	100	24	76
11	**1c**	CWP	96	97	3
12	**1c**	PCWP	100	0	100

a) Sulfide (2 mmol), 35% H_2O_2 (4 mmol) and catalyst (0.5 mol%) were reacted in $CHCl_3$ (30 ml) at room temperature for 2 h.
b) Determined by HPLC.

These catalysts were subjected to IR, ^{31}P-NMR9) and combustion analyses in order to establish the physicochemical properties of these catalysts. The results are summarized in Table 2. The analytical data of the H-CMP catalyst, obtained by treating CMP with excess 35% H_2O_2,10) was very different from those of the original CMP, and they were closely resemble to those of PCMP.11) On the other hand, the analytical data of the H-CWP, obtained by the same treatment as above using CWP in place of CMP, were very similar to those of the original CWP.

These facts suggest that CMP is easily reconstructed to PCMP upon treatment with H_2O_2. However, CWP, which is considered to be more stable than CMP, maintains the structure closed to Keggin unit after treatment with H_2O_2.

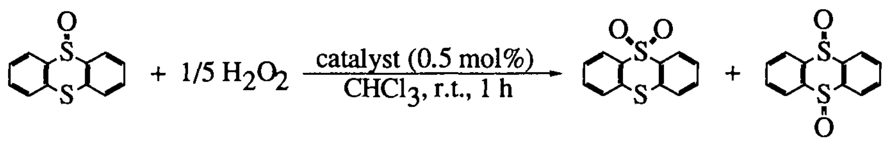
The difference in selectivity by CWP and PCWP-catalyzed oxidations of **1** appears to reflect the oxidizing potential of the peroxo species generated from CWP and PCWP with H_2O_2 in the catalytic cycle. The oxidation results indicate that the reactivity of the peroxo species derived from CWP is lower than that derived from PCWP. Therefore, it is believed that the oxidation of **1** by CWP stopped at the stage of the formation of sulfoxides.

Table 2. Analytical Data of Cetylpyridinium Molybdo- and Tungstophospates

Catalyst	Elemental Analysis / %			IR / cm^{-1}	^{31}P-NMR / ppm b)
	C	H	N		
CMP	27.76	3.24	1.18	1062, 956, 878, 800	-3.03
H-CMP a)	44.52	7.01	2.46	988, 874, 588, 541	7.74
PCMP	43.89	7.07	2.46	987, 874, 588, 542	7.74
CWP	19.94	3.08	1.22	1079, 977, 893, 807	-14.50
H-CWP a)	19.94	3.41	1.23	1079, 977, 893, 808	-14.34
PCWP	36.18	5.48	1.99	949, 836, 572, 549	7.36

a) H-CMP and H-CWP were obtained after treatment of CMP and CWP (0.18 mmol) with 35% H_2O_2 (5 ml) at 40°C for 48 h, respectively.
b) 85% H_3PO_4 was used as the external standard.

Furthermore, in the oxidation of thianthrene 5-oxide (**4**) by CWP and PCWP, the result was markedly different from each other (Scheme 2).12) Although the oxidation of **4** by CWP occurred with difficulty, **4** was converted into 5,5-dioxide (**5**) and 5,10-dioxide (**6**) by PCWP in good yield.



4 **5** **6**

Catalyst	Conv. / % a)	Selectivity / % b)	
		5	**6**
CWP	trace	-	-
PCWP	80	56	44

a) Based on the H_2O_2 used.
b) Determined by HPLC.

Scheme 2.

These results lead to the conclusion that the peroxo species derived from CWP and H_2O_2 in the catalytic cycle is vertually different from that derived from PCWP and H_2O_2, and the oxidizing potential of the former peroxo species is milder than that of the latter one.

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10) CMP or CWP (0.18 mmol) was stirred in excess 35% H_2O_2 (5 ml) at 40 °C for 48 h. After cooling the mixture to room temperature, the reaction mixture was filltered off. The resulting precipitate was washed with distilled water and dried *in vacuo*.

11) Recently, the crystal structure of $Q_3\{PO_4[Mo(O)(O_2)_2]_4\}$ (Q^+ = tetrahexylammonium), which is the same complex class of the PCMP, was determined by X-ray diffraction analysis; see Ref. 4.

12) Thianthrene 5-oxide (**4**) (1 mmol) was allowed to react with 35% H_2O_2 (0.2 mmol) in the presence of catalyst (0.5 mol%) in $CHCl_3$ (30 ml) at room temperature for 1 h. The product ratios were determined by HPLC analysis.

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