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Preparation, characterization and catalytic oxidation properties of bis-quaternary ammonium peroxotungstates and peroxomolybdates complexes

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Several novel kinds of bis-quaternary ammonium peroxotungstates and peroxomolybdates, such as $PhCH_2N(CH_2CH_2)_3NCH_2Ph[W_2O_3(O_2)_4]$, $PhCH_2N(CH_2CH_2)_3NCH_2Ph$ $[Mo_2O_3(O_2)_4]$, $[PhCH_2(CH_3)_2NCH_2]_2[W_2O_3(O_2)_4]$ and $[PhCH_2(CH_3)_2NCH_2]_2[Mo_2O_3(O_2)_4]$, have been synthesized and characterized by elemental analysis, IR and Raman spectroscopy. Their catalytic properties in mild oxidation of benzyl alcohol and ring-substituted benzyl alcohols were investigated with aqueous 30% H_2O_2 under halide- and organic solvent-free conditions. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: peroxotungstate; peroxomolybadate; bis-quaternary ammonium; clean oxidation; hydrogen peroxide

INTRODUCTION

In the age of advocating green chemistry, clean production and atomic economy, the oxidation of organic substrates by aqueous H_2O_2 has aroused the curiosity of chemical researchers.[1–5] Compared with traditional oxidants, hydrogen peroxide is a clean and environmentally friendly oxidant, because water is the only expected byproduct and it is easy to deal with after reactions. Meanwhile, dilute aqueous H_2O_2 (concentration less than 60%) is safe, non-toxic and low-cost. However, a metal catalyst is often required owing to its oxidant ability and insolubility in most organics. Accordingly, great effort has been devoted to searching for efficient catalysts that can activate but not decompose hydrogen peroxide.[6–11]

As an important class of reactive intermediates in catalytic oxidation reactions, peroxo transition metal complexes have attracted considerable attention. The systems of peroxomolybadates or peroxotungstates and phase transfer catalysts have been proved to be effective catalysts to activate hydrogen peroxide in selective oxidation reactions, such as epoxidation of olefin,[12–15] cleavage of double bonds[16] and conversion of primary and secondary alcohols to carbonyl compounds under moderate condition.[17,18] The reported peroxo complexes of molybdate and tungstate include mononuclear anion $[M(O_2)_4]^{2-}$, binuclear anion $[M_2O_3(O)_4]^{2-}$, mononuclear anion formed from molybdenum or tungstate and organic ligands, heteropolyperoxo-tungstate anion $\{PO_4[W(O)(O_2)_4]_4\}^{3-}$ and Keggin unit $[PW_{12}O_{40}]^{3-}$.[19,20] The cations in the complexes are all univalent quaternary phosphoniums or their ammonium analogs. From the viewpoint of electrostatic attraction, the association between a bivalent cation and a dianion is more extensive than that between a univalent cation and a dianion. As a result, the bivalent cation in the organic phase can easily extract dianion from the water phase. This principle could be applied to extract dianions of peroxomolybate into the organic phase, where oxidation reaction of organic substrates such as alcohols and olefins, occurs. If so, the catalytic oxidation may be possible in a water–oil diphase system.

Considering the above viewpoint, we have synthesized four novel bis-quaternary ammonium salts of binuclear peroxotungstate and peroxomolybdate complexes in which the cation and counteranion are all bivalent: $PhCH_2N(CH_2CH_2)_3NCH_2Ph[W_2O_3(O_2)_4]$, $PhCH_2N(CH_2CH_2)_3NCH_2Ph$ $[Mo_2O_3(O_2)_4]$, $[PhCH_2(CH_3)_2$

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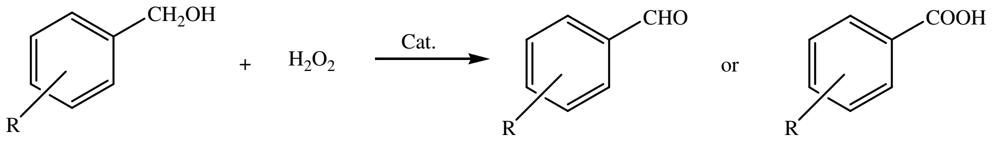

Scheme 1. Oxidation of alcohol.

$NCH_2]_2[W_2O_3(O_2)_4]$ and $[PhCH_2(CH_3)_2NCH_2]_2[Mo_2O_3(O_2)_4]$. The catalytic properties of bis-quaternary ammonium peroxo complexes were examined for the oxidation of benzyl alcohol and its ring-substituted derivations under mild conditions without organic solvents and halide (Scheme 1), because the oxidation of benzyl alcohol is a reaction of great commercial importance due to the extensive application of oxidizing products in the perfumery, pharmaceutical, dyestuff and agrochemical industries. Compared with univalent analogs, the synthesized complexes display preferable catalytic activities.

EXPERIMENTAL

Materials and instruments

Benzyl alcohol, potassium tungstate dihydrate, potassium molybdate dihydrate, 4-methylbenzyl alcohol, 4-nitrobenzyl alcohol, 2,4,6-trimethyl benzyl alcohol, 1,4-diazabicyclo^{2,2,2} octane, *N*,*N*,*N*′,*N*′-tetramethyl ethylenediamine and benzyl chloride were used as purchased. The 30% hydrogen peroxide was of AR grade and was titrated using a standard $KMnO_4$ solution, which was standardized with primary standard-grade $Na_2C_2O_4$ before use.

C, H and N element analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The active O was determined by titration of $KMnO_4$ solution. Mo and W were analyzed by gravimetrically. IR and Raman spectra were recorded separately on a Bruker Equinox-55 spectrophotometer (KBr pellets in the range 400–4000 cm^{-1}) and a Nicolet Almega Dispersive laser Raman spectrophotometer.

Synthesis of bis-quaternary ammonium

1,4-Dibenzyl-1,4-diazoniabicyclo^{2,2,2} octane dichloride(I) (Figure 1): 2.2 g (0.01 mol)1,4-diazabicyclo^{2,2,2} octane hexahydrate and 3.36 ml (3.80 g, 0.03 mol) benzyl chloride in 15 ml absolute ethanol were refluxed for 2 h. After being cooled to room temperature, anhydrous ether was added to precipitate the product as white powder crystal (2.08 g, yield 54.3%). Anal. calcd for $C_{20}H_{26}N_2Cl_2 \cdot H_2O$: C, 62.66; H, 7.36; N, 7.31; found: C, 62.78; H, 8.05; N, 7.30.

The method to synthesize *N*,*N*,*N*′,*N*′-tetramethyl-*N*,*N*-dibenzyl ethylenediamine dichloride(II) (Figure 2) was similar to that of 1,4-dibenzyl-1,4-diazoniabicyclo^{2,2,2} octane dichloride. The white powder crystal was obtained with 61.1% yield. Calcd for $C_{20}H_{30}N_2Cl_2$: C, 65.03; H, 8.19; N, 7.58; found: C, 64.78; H, 8.24; N, 7.44.

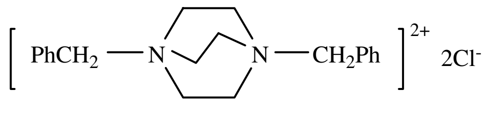

Figure 1. Structure of bis-quaternary ammonium(I).

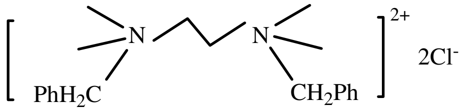

Figure 2. Structure of bis-quaternary ammonium(II).

Synthesis of peroxo complexes

$PhCH_2N(CH_2CH_2)_3NCH_2Ph[W_2O_3(O_2)_4]$(I): 5 ml 30% H_2O_2 was added to the solution of $K_2WO_4 \cdot 2H_2O$ (0.362 g, 1 mmol) in 5 ml water while being stirred at room temperature;[21,22] the resulting yellow solution was treated with dilute hydrochloric acid until it just turned colorless. A 0.383 g (1 mmol) aliquot of 1,4-dibenzyl-1,4-diazoniabicyclo^{2,2,2} octane dichloride in 5 ml water was added to the above mixture with stirring. After being allowed to stand for 5 min, the complex of $PhCH_2N(CH_2CH_2)_3NCH_2Ph[W_2O_3(O_2)_4]$ was precipitated as a white solid. Then it was filtered off, washed with water and dried over silica gel in a desiccator under vacuum.

The preparation of the complexes $PhCH_2N(CH_2CH_2)_3NCH_2Ph[Mo_2O_3(O_2)_4]$ (II), $[PhCH_2(CH_3)_2NCH_2]_2[W_2O_3(O_2)_4]$ (III), $[PhCH_2(CH_3)_2NCH_2]_2[Mo_2O_3(O_2)_4]$ (IV), $(C_{16}H_{33}NC_5H_5)_2[W_2O_3(O_2)_4]$ (V) and $(C_{16}H_{33}NC_5H_5)_2[Mo_2O_3(O_2)_4]$ (VI) was similar to the complex I.

General procedure of catalytic oxidation experiments

Oxidation of alcohols to aldehyde

To a 100 ml three-necked flask equipped with a condenser and a thermometer, a calculated amount of one of the complexes, benzyl alcohol and whole amount of 30% aqueous H_2O_2 were added in a molar ratio of 1 : 100 : 120. The reaction mixture was stirred electromagnetically at 90–95 °C for 8–12 h. After the reaction, the resulting mixture was cooled to room temperature, extracted with diethyl ether and dried by anhydrous Na_2SO_4. Then the extracts were evaporated to dryness. The quantitative product was dissolved in the minimum volume of methanol and the solution was treated

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with 2,4-dinitrophenylhydrazine in methanol to yield hydrazone derivatives. The hydrazone derivatives was filtered off, washed with cold water and dried to constant weight.[23]

Oxidation of alcohol to acid

The mixture of complex–alcohol–hydrogen peroxide in a molar ratio of 1 : 100 : 300 was stirred vigorously at 90–95 °C for 12–16 h, then cooled to room temperature. The white crystalline powder of acid was filtered off, and dried over $CaCl_2$ in a desiccator. The melting points of benzyl acid, *p*-toluic acid and 4-nitrobenzoic acid are 120.2–122.0, 180.3–182.9 and 237.1–241.5 °C, respectively.

RESULTS AND DISCUSSION

Composition and character of the complexes

The complexes had satisfactory element analytic results and coincided with their calculated values (Table 1). Because of the presence of peroxo group, which is liable to decompose after standing in light for a long time, the complexes must be kept in the dark and at low temperatures. The proposed structure of binuclear peroxo anions was reported by Bailey (Fig. 3).[22]

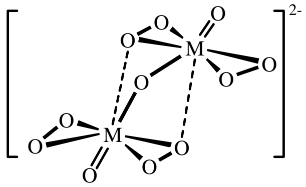

Figure 3. Proposed structure of the binuclear anion.

Infrared spectra and laser Raman spectra of the complexes

The IR and laser Raman spectra of complexes were similar to those of previously reported peroxo tungstate and molybdate derivatives.[22,23] The data of their IR and Raman spectra are listed in Table 2. The presence of strong bands around 820 in both the IR and Raman spectra is attributable to stretching vibrations of peroxy group O–O. These data are near the vibration of O–O in hydrogen peroxide at 877 cm^{-1}. The characteristic frequency in the stretching vibrations of these compounds appearing between 500 and 650 cm^{-1} is attributed to the existence of $\nu_{sym}[M(O_2)]$ and $\nu_{asym}[M(O_2)]$. The above stretching vibrations strongly suggest the presence of O–O in the complexes. The stretching vibrations of $\nu_{asym}(M_2O)$ and $\nu_{sym}(M_2O)$ could be observed near 700 and 450 cm^{-1}, respectively and their intensity mainly depends on the angles of M–O–M.

Catalytic ability of the complexes

The results of these complexes catalyzing 30% H_2O_2 to oxidize benzyl alcohol and its derivations to aldehyde or acid are

Table 1. The elemental analyses of the bis-quaternary annonium salts

Complex	Yield	C (calc.)	H (calc.)	N (calc.)	M (calc.)	O_2^{2-} (calc.)
I	60.72	28.51 (28.66)	3.09 (3.13)	3.31 (3.34)	43.16 (43.87)	15.89 (15.27)
II	74.45	36.15 (36.27)	3.89 (3.96)	4.13 (4.23)	28.13 (28.97)	18.85 (19.33)
III	69.76	28.00 (28.52)	3.57 (3.59)	3.21 (3.33)	43.08 (43.66)	14.76 (15.20)
IV	77.64	36.42 (36.05)	4.58 (4.54)	4.14 (4.20)	28.22 (28.80)	18.73 (19.21)
V	49.18	43.92 (43.76)	6.39 (6.64)	2.17 (2.43)	31.34 (31.90)	11.53 (11.10)
VI	45.29	51.39 (51.64)	7.53 (7.84)	2.59 (2.87)	19.13 (19.64)	13.48 (13.10)

Table 2. IR and Raman spectral data for the Mo(VI) and W(VI) complexes [band maxima (cm^{-1})]

Complex		$\nu(M{=}O)$	$\nu(O{-}O)$	$\nu_{sym}[M(O_2)]$	$\nu_{asym}[M(O_2)]$	$\nu_{sym}(M_2O)$	$\nu_{asym}(M_2O)$
I	IR	946	839	613	533		705
	Raman	950	853	619	558	430	716
II	IR	939	862	619	536		729
	Raman	940	851	575	550	430	727
III	IR	959	857	587	541		702
	Raman	963	869	619	552	436	714
IV	IR	965	858	590	537		731
	Raman	969	873	620	559	427	731
V	IR	954	839	616	568	456	687
	Raman	924	843	646	555		
VI	IR	968	858	637	587	403	695
	Raman	976	873	646	561		

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Table 3. Catalytic activities of the different catalysts in the oxidation of benzyl alcohol derivations (10.0 mmol)[a]

Complexes	Substrates	Products	Yield (%)
I	Benzyl alcohol	Benzylaldehyde	90.51
II	Benzyl alcohol	Benzylaldehyde	82.82
III	Benzyl alcohol	Benzylaldehyde	91.10
IV	Benzyl alcohol	Benzylaldehyde	88.31
V	Benzyl alcohol	Benzylaldehyde	81.86
VI	Benzyl alcohol	Benzylaldehyde	77.40
I	Benzyl alcohol	Benzoic acid	65.37
II	Benzyl alcohol	Benzoic acid	64.91
V	Benzyl alcohol	Benzoic acid	60.22
VI	Benzyl alcohol	Benzoic acid	58.35
I	4-Methylbenzyl alcohol	*p*-Tolualdehyde	87.88
II	4-Methylbenzyl alcohol	*p*-Tolualdehyde	80.34
I	4-Methylbenzyl alcohol	*p*-Toluic acid	50.47
II	4-Methylbenzyl alcohol	*p*-Toluic acid	55.51
I	4-Nitrobenzyl alcohol	4-Nitrobenzylaldehyde	75.23
II	4-Nitrobenzyl alcohol	4-Nitrobenzylaldehyde	74.21
I	4-Nitrobenzyl alcohol	4-Nitrobenzoic acid	71.27
II	4-Nitrobenzyl alcohol	4-Nitrobenzoic acid	69.45
I	2,4,6-Trimethylbenzyl alcohol	—	—
II	2,4,6-Trimethylbenzyl alcohol	—	—

[a] Reaction conditions: catalyst 0.1 mmol (1 mol%), H_2O_2 12 mmol for aldehyde and 30 mmol for acid, reaction temperature 90–95 °C.

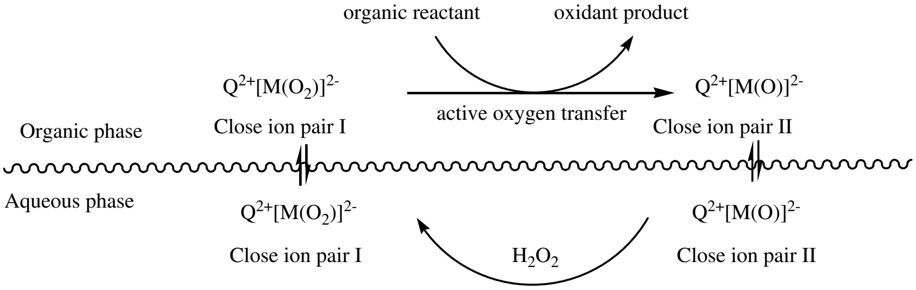
listed in Table 3. The data in Table 3 show that benzaldehyde can be obtained in high yield in the presence of six peroxo complexes when the mixture of complex, H_2O_2 and alcohol (in a ratio of 1 : 120 : 100) was stirred vigorously in air and at 90–95 °C for 8–12 h. The maximum yields of benzaldehyde can reach 91.10%. Control experiments indicate that, in the absence of the bis-quaternary ammonium peroxo complexes, the oxidation of benzyl alcohol gives benzaldehyde in rather a low yield of 11%. It is noteworthy that, from Table 1, it appears that the catalytic activities of univalent quaternary ammoniun complexes V and VI are less effective than that of bisquaternary ammoniun complexes for the oxidation of benzyl alcohol under the same reaction conditions. Although the oxidation reaction occurred in the presence of complexes V and VI, compared with bisquaternary ammoniun complexes, the yields of benzylaldehyde and benzoic acid are all lower.

The ring-substituted benzyl alcohol can also be oxidized to aldehyde. Even 4-methylbenzyl alcohol, considered difficult to oxidize, gave *p*-tolualdehyde in 87.88% yield. Moreover, the catalytic activities of complex III and IV are superior to that of complexes I and II respectively. The reason may be the rigid structure of cation in the latter. Despite that, there is a very slight difference in their catalytic efficiency; the Mo(VI) complexes were less active than analogous W(VI) complexes except in the oxidation of 4-methylbenzyl alcohol to *p*-toluic acid, which is consistent with some of the previous reports.[24,25] We speculated that it very likely resulted from the nature of the metal atom.

Although the yield of acid is a little low, benzyl alcohol and substituted benzyl alcohol can be converted to acid when the ratio of H_2O_2 and alcohol is changed from 1 : 1.2 to 1 : 3.0. The yield of acid is influenced by the characteristics of the substituent. The electron-withdrawing group of nitro decreases the electron cloud density of carbonyl, thus the catalyst with the nucleophilic peroxo group accesses carbonyl electron easily. Therefore, the yield of 4-nitrobenzoic acid is the highest, whereas, on the contrary, the yield of *p*-toluic acid is the lowest due to the electron-donating group of methyl. In addition, the oxidation of 2,4,6-trimethylbenzyl alcohol cannot obtain the corresponding aldehyde or acid under the same condition. The reason may lie in the influence of steric effect. The presence of the two neighbor groups of methyls results in a crowded condition around hydroxylmethyl, which makes it difficult for the peroxo complex to approach 2,4,6-trimethylbenzyl alcohol. Thus, the oxidation reaction cannot take place.

Reaction catalytic cycle

Based on the results of experiment, we proposed a possible catalytic cycle, given in Scheme 2, for the biphase oxidation as we described in our reported paper.[26] Because of the many interactions in the complexes, such as ionic interaction, intramolecular and intermolecular hydrogen bonds,[27] a close ion pair was formed between bis-quaternary ammonium bivalent cation (Q^{2+}) and peroxo metal dianion $[W(O_2)]^{2-}$. We inferred that the close ion pair I parted between the aqueous phase and organic phase. The anion $[W(O_2)]^{2-}$ in the



Scheme 2. Suggested catalytic cycle of the oxidation.

organic phase transferred its active oxygen to organic reactant and generated oxidant product. During the transfer of active oxygen, the deperoxotungstate $[W(O)]^{2-}$ was produced. At the same time, the close ion pair II, which also parted between the aqueous phase and organic phase, was formed from Q^{2+} and the anion of deperoxotungstate $[W(O)]^{2-}$. In the aqueous phase, the H_2O_2 and deperoxotungstate anion $[W(O)]^{2-}$ were combined to produce close ion pair I again. The transfer of active oxygen took place once more after close ion pair I entered the organic phase. Thereby, the catalytic cycle was finished. In this way, bis-quaternary ammonium cation can extract peroxo Mo (VI) and W(VI) dianion carrying active oxygen into organic phase where the oxidation reaction takes place effectively. Thus, the oxidation reactions proceed successfully between two phases and the yield of the products is enhanced. Moreover, the bis-quaternary ammonium cations possessing lipophilic nature play an important role in the catalytic oxidation reaction because they can extract water-soluble peroxo dianion from aqueous to organic phase depending on close combination with dianion.

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