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RESEARCH ARTICLE

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Synthesis of bis-quaternary ammonium peroxotungstates (peroxomolybdates) and their catalytic activity in oxidation of alcohols by aqueous H_2O_2

Abstract Three kinds of bis-quaternary ammonium salts of peroxotungstate and peroxomolybdate, such as $PhCH_2N(CH_2)_6NCH_2Ph[W(O_2)_4]\cdot 2H_2O$, $PhCH_2N(CH_2)_6NCH_2Ph[WO(O_2)_2(C_2O_4)]$ and $PhCH_2N(CH_2)_6NCH_2Ph[MoO(O_2)_2(C_2O_4)]$, have been synthesized and characterized. Their catalytic activity in the oxidation of cyclohexanol and benzyl alcohol was investigated with only aqueous 30% hydrogen peroxide. The results show that the bis-quaternary ammonium peroxotungstates are excellent catalysts in the oxidation of benzyl alcohol and cyclohexanol under moderate conditions. However, the catalytic ability of bis-quaternary ammonium peroxomolybadates is relatively poor. The yields of benzyl acid, benzaldehyde, and cyclohexanone reached up to 93.0%, 93.6%, and 91.7%, respectively.

Keywords peroxotungstate, peroxomolybadate, bis-quaternary phosphonium, hydrogen peroxide

Aqueous H_2O_2, especially a concentration of less than 60%, has been known as a kind of clean and ideal oxidant due to its properties of being safe, non-toxic, and low-cost. Moreover, water is the only expected byproduct and it is easy to be dealt with after reactions. In recent years, the replacement of hydrogen peroxide as a benign oxidant to the traditional oxidant such as Cr(VI) compounds, $KMnO_4$, HNO_3, etc., has been highly regarded and prompted continuous interest of academic and industrial groups [1,2]. However, aqueous H_2O_2 is a moderate inorganic oxidant, and it allows aqueous—organic diphase system with most organics. Another problem of aqueous H_2O_2 as oxidant stems from its poor stability because it is liable to decompose when heated or in the presence of many metal ions, non-metal ions, and finely ground particles. Therefore, there is a competition between the decomposition and oxidation reaction. The above disadvantages of aqueous H_2O_2 limit its application in organic oxidation reactions. Therefore, the key problem of the relevant research is to search for efficient catalysts that can activate but not decompose H_2O_2 [3].

The multiple catalytic system of peroxomolybdates or peroxotungstates and phase transfer catalysts has been proved to be efficient catalysts in epoxidation of olefin [3–9], cleavage of double bond [8,10–13], conversation of primary and secondary alcohol to carbonyl compounds with aqueous H_2O_2 as oxidant under moderate condition [14,15]. The reported peroxo complexes of molybdate and tungstate are involved in mononuclear anion $[M(O_2)_4]^{2-}$, dinuclear anion $[M_2O_3(O)_4]^{2-}$, mononuclear anion formed from molybdenum or tungstate and organic ligands $[WO(O)_2L_{(2)}]^{2-}$, heteropolyperoxotungstate anion $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$, $[PW_{12}O_{40}]^{3-}$, etc. The phase transfer catalyst in the catalytic system is univalent quaternary phosphonium or ammonium and the cations in the complexes are all univalent quaternary phosphoniums or their ammonium analogs, on the contrary, the peroxo anion is polyvalent. For the sake of poor association between univalent cation and polyvalent anion, the peroxo anion with active oxygen atoms cannot be extracted into organic phase effectively by univalent cation. Consequently, the oxidation reactions cannot proceed successfully in the aqueous—organic diphase system. We noticed that the diammonium salt of 1, 4-distearyl-1, 4-diazabicyclo [2,2,2] octane can extract dianion species into organic phase selectively from the aqueous phase that contain both monoanion and dianion [16]. The basic reason rests with that 1, 4-distearyl-1, 4-diazabicyclo [2,2,2] octane possesses two positive charges, which form two recognizing sites for dianions. In the viewpoint of electrostatic attraction, it is self-evident that close association was brought into between bivalent cation and dianion. As a result, the bivalent cation in the organic phase can extract dianion from the water phase easily. We presume that this principle could be applied to extract dianion of peroxomolybate into the organic phase, where organic substrate such as alcohols, olefins, etc., occurs. If so, the catalytic oxidation was prospected to carry out perfectly in the water—oil diphase system.

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Taking the above viewpoint into consideration, we have developed three bis-quaternary ammonium complexes of peroxotungstate and peroxomolybdate in which the cation and counteranion are all bivalent: $PhCH_2N(CH_2)_6NCH_2Ph[W(O_2)_4]\cdot 2H_2O$, $PhCH_2N(CH_2)_6NCH_2Ph[WO(O_2)_2(C_2O_4)]$, and $PhCH_2N(CH_2)_6NCH_2Ph[MoO(O_2)_2(C_2O_4)]$. Their catalytic abilities were investigated in the oxidation reaction of cyclohexanol to cyclohexanone and benzyl alcohol to benzaldehyde using 30% H_2O_2 as oxidant under organic solvent- and halide-free conditions.

1 Experiments

1.1 Materials and apparatus

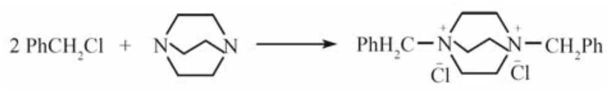
C, H, N element analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The active O was determined by titration of $KMnO_4$ solution, infrared (IR), and Raman spectra were recorded separately on a Bruker EQUINOX-55 spectrophotometer (KBr pellets in the range 400–4000 cm^{-1}) and a Nicolet Almega Dispersive laser Raman spectrophotometer. Melting point was determined on a WRS-1 apparatus and uncorrected. The molar conductivities were determined according to a standard method.

Cyclohexanol, benzyl alcohol, $Na_2WO_4\cdot 2H_2O$, $Na_2MoO_4\cdot 2H_2O$, oxalic acid, benzyl chloride, and 2,4-dinitrophenylhydrazine, 1,4-diazabicyclo [2,2,2] octane hexahydrate were used as purchased. 30% hydrogen peroxide was of A. R. grade and was titrated by a standard $KMnO_4$ solution, which was standardized with primary standard grade $Na_2C_2O_4$ before use. $K_2[WO(O_2)_2(C_2O_4)]$, $K_2[MoO(O_2)_2(C_2O_4)]$ were synthesized according to the reference [17].

1.2 Synthesis of bis-qaternary ammonium

1.10 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 cooling to room temperature, anhydrous ether was added to precipitate the product as white powder crystal with a 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.

1.3 Synthesis of peroxo complexes



$PhCH_2N(CH_2)_6NCH_2Ph[W(O_2)_4]\cdot 2H_2O$ (I): 5 mL of 30% aqueous H_2O_2 was added slowly to the solution of 0.66 g (2.0 mmol) $Na_2WO_4\cdot 2H_2O$ in 5 mL of water while stirring and cooling by ice water. Then, 0.766 g (2 mmol) 1, 4-dibenzyl-1, 4-diazoniabicyclo [2, 2, 2] octane dichloride in 5 mL water was added to the above solution under stirring. After continuing to stir for another 20 min, the mixture was allowed to stand overnight at 5°C. The complex of $PhCH_2N(CH_2)_6NCH_2Ph\ [W(O_2)_4]\cdot 2H_2O$ was precipitated as a yellow microcrystalline.

The preparation methods of $PhCH_2N(CH_2)_6NCH_2Ph[WO(O_2)_2(C_2O_4)]$ (II), $PhCH_2N(CH_2)_6CH_2NPh[MoO(O_2)_2(C_2O_4)]$ (III) were similar to complex (I) [10].

1.4 General procedure of catalytic oxidation experiments

Synthesis of benzaldehyde (cyclohexanone): the mixture of complex I, benzyl alcohol (cyclohexanol), and 30% hydrogen peroxide in a molar ratio of 1:100:120 was stirred drastically at 80°C for 8 to 12 h. After cooling to room temperature, the organic phase was separated from the reaction mixture and dried by anhydrous Na_2SO_4. The quantitative product was dissolved in the minimum volume of methanol and the solution was treated 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.

Synthesis of benzonic acid: the mixture of complex I, benzyl alcohol, and 30% hydrogen peroxide in a molar ratio of 1: 100: 220 was stirred drastically at 80°C for 8 to 12 h. The white crystalline powder of the acid appeared, after the reaction mixture was cooled to room temperature. The melting point of benzyl acid is 120.2–122.0°C (Reference value: 122–123°C).

The processes of complexes II and III catalyzing H_2O_2 to oxidize benzyl alcohol and cyclohexanol were similar to complex I.

2 Results and discussion

2.1 The composition and character of the complexes

The satisfactory element analytical results of the complexes are listed in Table 1. The determination of the complexes' molar conductivities indicates that although they are 1:1 electrolyte, their molar conductivities are lower than the data of common 1:1 electrolyte (Geary recommended [18] that the molar conductivities of 1:1 electrolyte varied from 23 to 42 $S\cdot cm^2\cdot mol^{-1}$ in DMSO). The reason may result in that the complexes cannot sufficiently ionize in the solution because of extensive association between the dication of bis-quaternary ammonium and the dianion of peroxomolybdates and peroxotungstates.

2.2 Infrared (IR) and laser Raman spectra of the complexes

The IR and laser Raman spectra data of these complexes are summarized in Table 2. It is reported that the sodium or potassium salts containing $[W(O_2)_4]^{2-}$ are highly explosive, it is difficult to obtain their IR spectra, in particular, Raman

Table 1 The elemental analysis and molar conductivity (DMSO 25°C) of bis-quaternary ammonium salts

Complex	Elemental analysis / %				Molar conductivity / $S \cdot cm^2 \cdot mol^{-1}$
	C (cal.)	H (cal.)	N (cal.)	O_2^{2-} (cal.)	
I	38.22(38.48)	4.26(4.520)	4.41(4.48)	20.83(20.50)	10.5
II	40.79(40.89)	4.0(4.05)	4.33(4.23)	9.56(9.56)	15.8
III	46.51(47.32)	4.66(4.690)	4.96(5.0)	11.46(11.02)	17.3

spectra [19]. The reason may be that the peroxo complexes are unstable under the determination condition with laser as lamp-house. There are a few reports about the IR spectra of the peroxo complex $[W(O_2)_4]^{2-}$. But one kind of crystalline complexes of $[W(O_2)_4]^{2-}$ was obtained from $[W(O_2)_4]^{2-}$ and bis-quaternary ammonium, which are stable enough to obtain their Raman spectra and IR spectra under the determined condition. Thus, the laser Raman spectrum of the $[W(O_2)_4]^{2-}$ complexes in solid state was obtained successfully.

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

Complex		v (M = O)	v (O–O)	$v_{sym}[M(O_2)]$	$v_{asym}[M(O_2)]$
I	IR	□	853	592	550
	Raman	□	852	620	532
III	IR	941	863	638	526
	Raman	941	843	621	521
III	IR	934	853	648	515
	Raman	933	863	621	538

It can be seen from Table 2, that the complexes display the analogous strong stretching vibrations frequency of IR and Raman spectra. The stretching vibrations near 950 cm^{-1} were assigned to the presence of M = O but not oxalate [20]. The presences of strong bands observed in the region from 800 to 900 cm^{-1} in all complexes, are attributable to the presence of O–O in the complexes, which is close to the stretching vibrations frequency of the peroxo group in H_2O_2. The stretching vibrations of $v_{asym}(M_2O)$ and $v_{sym}(M_2O)$ could be observed in the region from 650 cm^{-1} to 500 cm^{-1}.

2.3 Catalytic ability of the complexes

The effects of the bis-quaternary ammonium peroxo complexes catalyzing 30% hydrogen peroxide to oxidize benzyl alcohol and cyclohexanol under aqueous-organic diphase system are illustrated in Table 3.

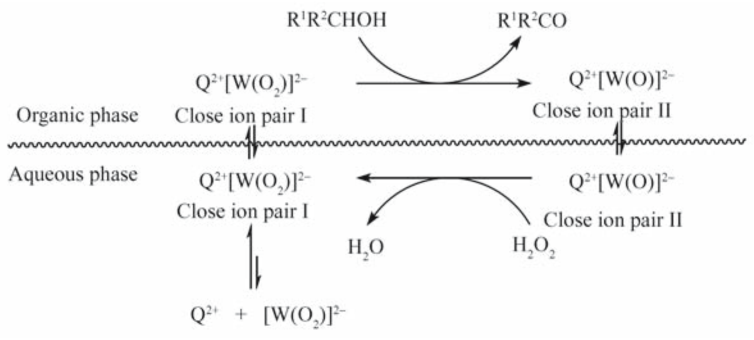
Table 3 Catalytic activity of different catalysts in the oxidation of alcohols

Complex	Alcohol	Product	Yield (%)
I	$C_6H_5CH_2OH$	$C_6H_5CO_2H$	88.8
	$C_6H_5CH_2OH$	C_6H_5CHO	85.3
	cyclo-$C_6H_{11}OH$	cyclo-$C_6H_{10}O$	90.2
II	$C_6H_5CH_2OH$	$C_6H_5CO_2H$	93.0
	$C_6H_5CH_2OH$	C_6H_5CHO	93.6
	cyclo-$C_6H_{11}OH$	cyclo-$C_6H_{10}O$	91.7
III	$C_6H_5CH_2OH$	$C_6H_5CO_2H$	39.2
	$C_6H_5CH_2OH$	C_6H_5CHO	57.8
	cyclo-$C_6H_{11}OH$	cyclo-$C_6H_{10}O$	32.9

The data in Table 3 show that benzaldehyde or cyclohexanone can be obtained in high yield in the presence of three peroxo complexes when the ratio of complex, H_2O_2, and alcohol is 1: 120: 100. The catalytic activity of complex II has an advantage over others and the Mo(VI) complex III was far less active than complex II. Moreover, it should be noted that benzyl alcohol could be converted selectively to acid through the adjustment of hydrogen peroxide amount used. Benzoic acid was obtained in high yield with the mixture of complex, H_2O_2, and benzyl alcohol in a molar ratio of 1: 220: 100. While a 4.4-fold excess of H_2O_2 was used in oxidation of cyclohexanol, a complicated mixture containing mainly adipic acid was obtained. The composition of the product is being studied. At the same time, when adopting complex II as catalyst, the yield of three products is higher than that under the same condition using $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$–$Na_2WO_4$ as catalytic oxidation system [21].

The contrast experiment indicated that the yield of corresponding oxidation product is rather low only using molybdate or tungstate as catalyst. The reason is that peroxomolybdate and peroxotungstate possess good solubility in aqueous and poor solubility in organic phase. Correspondingly, it is difficult for peroxo anion carrying active oxygen to enter organic phase, which make the oxidant reaction difficult to take place. But the yield of benzaldehyde and cyclohexanone has shown some enhancement with synthesized complex as catalyst. Accordingly, the bis-quaternary ammonium cations play an important role in the catalytic oxidation reaction.

There is no report of bivalent bis-quaternary ammonium in the peroxo peroxotungstate and peroxomolybdate complexes. It is generally believed that the strong binding force between the bis-quaternary ammonium and dianion prevents ionic exchange of different anion, thus the catalytic effect was confined. Although the cations and anions of complexes are unsusceptible to dissociate for the strong bondability between them, which was proved by the molar conductivities, they possess good catalyzed effect. That illuminates the catalytic mechanism is probably different from common mechanism. We speculated that the close ion pairs $Q^{2+}[W(O_2)]^{2-}$ were formed from bis-quaternary ammonium cation and peroxo anion, and this kind of close ion pair has certain solubility both in the aqueous and organic phase. Peroxo anions in organic phase transfer their active oxygens to substrate and produced oxidant product, simultaneously the new close ion pair $Q^{2+}[W(O)]^{2-}$ without active oxygen was formed, which also parted between the aqueous phase and organic phase. In the aqueous phase, the H_2O_2 and deperoxotungstate anion $Q^{2+}[W(O_2)]^{2-}$ were combined to produce close ion pair



Scheme 1 Suggested catalytic cycle of the oxidation

$Q^{2+}[W(O_2)]^{2-}$ again. Therefore, the catalytic cycle was finished. In this way, bis-quaternary ammonium cation can extract peroxo Mo(VI) and W(VI) dianion with active oxygen into organic phase, where the oxidation reaction was carried out effectively.

In conclusion, the bis-quaternary ammonium peroxomolybdates and peroxotungstates are effective catalysts in the oxidation of alcohol under diphase system with aqueous H_2O_2. Although the exact catalytic mechanism of these complexes is still unclear, the catalytic oxidation system takes on the characteristic of cleanness, safety and operational simplicity, and the yields of the product are high. Consequently, the oxidation method meets the needs of contemporary green chemistry and is suitable for practical organic synthesis.

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