

Oxidation of alcohols with H₂O₂ catalyzed by bis-quaternary phosphonium peroxotungstates (or peroxomolybdates) under halide- and organic solvent-free condition

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Abstract

Several novel kinds of bis-quaternary phosphonium salts of peroxotungstate and peroxomolybdate, such as Ph₃P(CH₂)₂PPh₃[W(O₂)₄]:2H₂O, Ph₃P(CH₂)₂PPh₃[WO(O₂)₂(C₂O₄):2H₂O, Ph₃P(CH₂)₃PPh₃[W(O₂)₄]:2H₂O, and Ph₃P(CH₂)₂PPh₃[MoO(O₂)₂(C₂O₄):2H₂O, have been synthesized and characterized by elemental analysis, IR and Raman spectroscopy. Their catalytic properties in oxidation of cyclohexanol and benzyl alcohol to cyclohexanone, benzaldehyde or benzoic acid were investigated with aqueous 30% hydrogen peroxide under halide- and organic solvent-free conditions. The results show that the bis-quaternary phosphonium peroxotungstates have excellent catalytic ability to the oxidation reaction of benzyl alcohol and cyclohexanol by hydrogen peroxide. The Mo(IV) analog peroxo complexes were less active than peroxotungstates. The maximum yields of benzaldehyde, benzoic acid and cyclohexanone can be reached 93.89%, 88.87%, and 92.70%, respectively.

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1. Introduction

Recently, more and more attention has been paid to the replacement of hydrogen peroxide as a green oxidant to the traditional oxidant such as Cr(VI) compounds, KMnO₄, HNO₃, and so on [1,2]. Hydrogen peroxide has many advantages as oxidant in oxidation reactions because water is the only expected side product and it is easy to be dealt with after reactions. Meanwhile, dilute aqueous hydrogen peroxide (concentration less than 60%) solution is safe, non-toxic and low-cost. However, aqueous hydrogen peroxide is a moderate inorganic oxidant, and it does not form a homogeneous solution with most organics. The other problem of aqueous

hydrogen peroxide as oxidant rises from its poor stability because it is liable to decompose while heated or in the presence of many metal ions, non-metal ions and finely ground particle. Therefore, there is a competition between the decomposition reaction and oxidation reaction. The above disadvantages of aqueous hydrogen peroxide limit its application in organic oxidation reactions. Accordingly, the key problem of relevant research is to look for efficient catalysts that can activate but not decompose hydrogen peroxide [3].

The system of peroxomolybdates or peroxotungstates and phase transfer catalysts has been proved as the most efficient catalysts, with hydrogen peroxide as oxidant, in epoxidation of olefin [3–9], cleavage of double bond [8,10–13], conversation of primary and secondary alcohol to carbonyl compounds under moderate condition [14,15]. The reported peroxo complexes of molybdate and tungstate include mononuclear anion [M(O₂)₄]²⁻, dinuclear anion [M₂O₃(O)₄]²⁻, mononuclear anion formed from molybde-

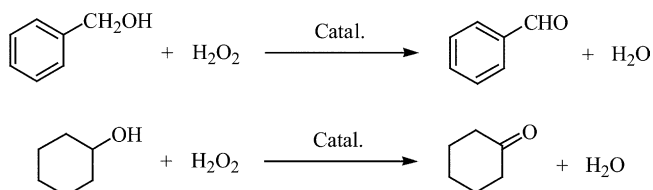
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num or tungstate and organic ligands, heteropolyperoxo-tungstate anion $\{\text{PO}_4[\text{W}(\text{O})(\text{O}_2)_2]_4\}^{3-}$ and $[\text{PW}_{12}\text{O}_{40}]^{3-}$, etc. The phase transfer catalyst in the reaction system is univalent quaternary phosphonium or ammonium. Owing to the poor association between univalent cation and multivalent anion, the peroxy anion carrying active oxygen atoms cannot enter organic phase effectively. Consequently, the oxidation reactions cannot proceed successfully in aqueous–organic biphasic system. We noted 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 containing both monoanion and dianion [16]. The reason is 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 obvious that the association between a bivalent cation and a dianion is so extensive that the bivalent cation in the organic layer can extract dianion from water layer easily. We suggest that this principle could be applied to extract dianion of peroxomolybdate, peroxotungstate or their complexes with organic ligands into organic layer, where oxidation reaction of organic substrate such as alcohols, olefins, etc., occurs. If so, the catalytic oxidation was prospectively to carry out perfectly in water–oil biphasic system.

Basing on the above considerations, we have synthesized four novel bis-quaternary phosphonium salts of peroxo-tungstate and peroxomolybdate in which the cation and counteranion are all bivalent: $\text{Ph}_3\text{P}(\text{CH}_2)_2\text{PPh}_3[\text{W}(\text{O}_2)_4]\cdot 2\text{H}_2\text{O}$, $\text{Ph}_3\text{P}(\text{CH}_2)_2\text{PPh}_3[\text{WO}(\text{O}_2)_2(\text{C}_2\text{O}_4)]\cdot 2\text{H}_2\text{O}$, $\text{Ph}_3\text{P}(\text{CH}_2)_3\text{PPh}_3[\text{W}(\text{O}_2)_4]\cdot 2\text{H}_2\text{O}$, and $\text{Ph}_3\text{P}(\text{CH}_2)_2\text{PPh}_3[\text{MoO}(\text{O}_2)_2(\text{C}_2\text{O}_4)]\cdot 2\text{H}_2\text{O}$. The catalytic ability of bis-quaternary phosphonium peroxomolybdates and peroxotungstates in the oxidation of cyclohexanol, benzyl alcohol was investigated without organic solvents and halide.



2. Experimental

2.1. Materials and apparatus

Cyclohexanol, benzyl alcohol, sodium tungstate dihydrate, sodium molybdate dihydrate, oxalic acid, ethylene bromide, trimethylene bromide were used as purchased. A 30% hydrogen peroxide was of A.R. grade and was titrated by a standard KMnO_4 solution, which was standardized with primary standard grade $\text{Na}_2\text{C}_2\text{O}_4$ before use. The molar conductivities were determined according to standard method using *N,N*-dimethylformamide and methanol as solvent. $\text{Ph}_3\text{P}(\text{CH}_2)_2\text{PPh}_3\text{Br}_2$ and $\text{Ph}_3\text{P}(\text{CH}_2)_3\text{PPh}_3\text{Br}_2$ were pre-

pared by known procedures [17,18]. $\text{K}_2[\text{WO}(\text{O}_2)_2(\text{C}_2\text{O}_4)]$ and $\text{K}_2[\text{MoO}(\text{O}_2)_2(\text{C}_2\text{O}_4)]$ were synthesized in term of the reference [19].

C and H 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 and a Nicolet Almega Dispersive laser Raman spectrophotometer. Melting point was determined on a WRS-1 apparatus and uncorrected.

2.2. Synthesis of peroxo complexes

$\text{Ph}_3\text{P}(\text{CH}_2)_2\text{PPh}_3[\text{W}(\text{O}_2)_4]\cdot 2\text{H}_2\text{O}$ (I): 0.66 g (2.0 mmol) of sodium tungstate dihydrate was dissolved in 5 mL of water, then, 5 mL of 30% aqueous hydrogen peroxide was added while stirring at room temperature. About 15 min later, the solution of 1.424 g (2.0 mmol) $\text{Ph}_3\text{P}(\text{CH}_2)_2\text{PPh}_3\text{Br}_2$ in 5 mL water was added while stirring. After allowed to stand for 5 min, the complex of $\text{Ph}_3\text{P}(\text{CH}_2)_2\text{PPh}_3[\text{W}(\text{O}_2)_4]\cdot 2\text{H}_2\text{O}$ was precipitated as a yellow microcrystalline solid. Then it was filtered off, washed with water and dried over silica-gel in a desiccator under vacuum. The elemental analyses and molar conductivities are listed in Table 1.

The preparation of the complexes $\text{Ph}_3\text{P}(\text{CH}_2)_3\text{PPh}_3[\text{W}(\text{O}_2)_4]\cdot 2\text{H}_2\text{O}$ (II), $\text{Ph}_3\text{P}(\text{CH}_2)_2\text{PPh}_3[\text{WO}(\text{O}_2)_2(\text{C}_2\text{O}_4)]\cdot 2\text{H}_2\text{O}$ (III), and $\text{Ph}_3\text{P}(\text{CH}_2)_2\text{PPh}_3[\text{MoO}(\text{O}_2)_2(\text{C}_2\text{O}_4)]\cdot 2\text{H}_2\text{O}$ (IV) was similar to the complex I.

2.3. General procedure of catalytic oxidation experiments

2.3.1. Oxidation of alcohols to carbonyl compounds

To a 100 mL three-necked flask equipped with a condenser and a thermometer, a calculated amount of one of the complexes described above, benzyl alcohol (or cyclohexanol) and a 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 80 °C for 8–12 h. After the reaction mixture was cooled to room temperature, organic phase was separated 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.

2.3.2. Oxidation of benzyl alcohol to benzoic acid

The mixture of the complex, benzyl alcohol, hydrogen peroxide in a molar ratio of 1:100:220 was stirred vigorously at 90 °C for 6 h, then cooled to room temperature. The white crystalline powder of benzoic acid was filtered off, dried over CaCl_2 in a desiccator. The melting point of the product is 120.2–122.0 °C.

Table 1
The elemental analyses and molar conductivities (DMF, 25) of the bis-quaternary phosphonium salts

Complex	Yield (%)	Elemental analyses (%)				Molar conductivity (S cm ² mol ⁻¹)
		C (cal.)	H(cal.)	M(cal.)	O ₂ ²⁻ (cal.)	
I	82.72	51.50 (50.69)	4.28 (4.25)	20.25 (20.41)	13.99 (14.22)	22.5
II	79.76	51.13 (51.08)	4.00 (4.07)	20.46 (20.10)	13.82 (14.00)	12.8 ^a
III	76.42	51.20 (51.22)	4.56 (4.41)	19.20 (19.54)	6.49 (6.80)	45.4
IV	87.67	56.44 (56.35)	4.47 (4.49)	11.29 (11.25)	7.20 (7.51)	47.1

^a Determined in methanol.

3. Results and discussion

3.1. The composition and character of the complexes

The complexes have the satisfactory element analytical results and coincide to their calculated values (Table 1). The molar conductivities determination of the complexes shows that, although they are 1:1 electrolyte, their molar conductivities without exception are lower than the data of common 1:1 electrolyte (Geary recommended [20] that the molar conductivities of 1:1 electrolyte varied from 65 to 90 S cm² mol⁻¹ in DMF and from 80 to 115 S cm² mol⁻¹ in the methanol). The reason is probably because the complexes cannot sufficiently ionise in the solution due to extensive association between the dication of bis-quaternary phosphonium and the dianion of peroxomolybdates and peroxotungstates.

3.2. The Infrared spectra and laser Raman spectra of the complexes

Because of complexes containing [W(O₂)₄]²⁻ possessing high explosively, it is difficult to obtain their infrared spectra and, in particular, Raman spectra [21]. Up to now, only a few reports about the infrared spectra of these complexes have been published yet. Most Raman spectra and infrared spectra of Mo or W concern the dimmeric species [M₂O₃(O₂)₄]²⁻. But using the bis-quaternary phosphonium as countercations, we obtained two kind of crystalline complexes of [W(O₂)₄]²⁻ which are stable enough to obtain their Raman spectra and infrared spectra under the determine condition. Thus, the laser Raman spectrum of the [W(O₂)₄]²⁻ complexes in solid state was obtained successfully. The data of their Raman spectra are listed in Table 1. However, standing in light for a long time, this complex also decomposed, so they must be kept in dark and at low temperature.

It can be seen from Table 2, that the complexes have the similar strong stretching vibrations frequency in the infrared and Raman spectra. The presences of strong bands observed in the region from 850 to 900 cm⁻¹ in both the infrared and Raman spectra of all the complexes, attributable to the symmetric and antisymmetric stretching vibrations of O–O and [M(O₂)], strongly suggest the presence of O–O in the complexes. These data is near the vibration of O–O in hydrogen peroxide at 877 cm⁻¹ [22]. Besides, the stretching vibrations frequency of O–O is related to the center atom and the ligands. The most characteristic frequency in the stretch-

ing vibrations of these compounds appear between 500 and 650 cm⁻¹ are attributed to the existence of $\nu_{\text{sym}}[\text{M}(\text{O}_2)]$ and $\nu_{\text{asym}}[\text{M}(\text{O}_2)]$ [23]. In addition, the stretching vibrations near the 950 cm⁻¹ was assigned to the presence of M=O for complexes III and IV. The stretching vibrations of M=O, however, disappear for the complexes I and II.

3.3. Catalytic ability of the complexes

The results of the bis-quaternary phosphonium peroxomolybdates and peroxotungsten catalyzing 30% hydrogen peroxide to oxidize benzyl alcohol to benzaldehyde or benzoic acid and cyclohexanol to cyclohexanone were listed in Table 3.

The data in Table 3 indicate that benzaldehyde and cyclohexanone can be obtained in high yield when the mixture of complex, H₂O₂, and alcohol (in a ratio of 1:120:100) was stirred vigorously in air and at 90 °C for 8 h. Complex I is superior to complexes II and III for the oxidation of alcohol, though there is a very slight difference in their catalytic efficiency for oxidation reaction among them. Moreover, the catalytic activity of complex III, which contains oxalate ligands is better than that of complex II. However, the Mo(VI) analogous complexes were far less active.

The oxidation of benzyl alcohol to benzaldehyde or to benzoic acid is dependent on the dosage of hydrogen peroxide alone. When a mixture of complex, H₂O₂, and benzyl alcohol in a 1:220:100 molar ratio was heated at 90 °C, benzoic acid was obtained as the main product. While a 4.5-fold excess

Table 2
IR and Raman spectral data for the Mo(VI) and W(VI) complex [band maxima (cm⁻¹)]

Complexes	$\nu(\text{M}=\text{O})$	$\nu(\text{O}-\text{O})$	$\nu_{\text{sym}}[\text{M}(\text{O}_2)]$	$\nu_{\text{asym}}[\text{M}(\text{O}_2)]$
I				
IR	–	821	593	538
Raman	–	851	613	549
II				
IR	–	829	595	523
Raman	–	853	615	555
III				
IR	943	832	582	523
Raman	940	845	614	533
IV				
IR	940	856	580	548
Raman	941	866	614	564

Table 3

Catalytic activities of different the catalysts in the oxidation of alcohols to carbonyl compounds or to acids cyclohexanone, benzaldehyde or to benzoic acid

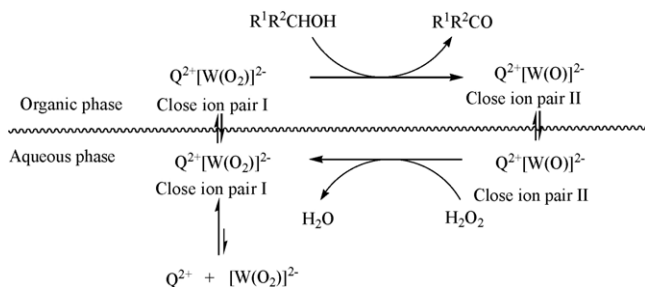
Complexes	Substrates	Products	Yield (%)
I	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CHO	93.89
	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CO ₂ H	88.87
	cyclo-C ₆ H ₁₁ OH	cyclo-C ₆ H ₁₀ O	92.70
	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CHO	75.76
II	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CO ₂ H	85.81
	cyclo-C ₆ H ₁₁ OH	cyclo-C ₆ H ₁₀ O	87.74
	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CHO	82.53
III	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CO ₂ H	90.07
	cyclo-C ₆ H ₁₁ OH	cyclo-C ₆ H ₁₀ O	91.73
	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CHO	37.50
IV	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CO ₂ H	48.57
	cyclo-C ₆ H ₁₁ OH	cyclo-C ₆ H ₁₀ O	32.90

of H₂O₂ was used in oxidation of cyclohexanol, that is, the molar ratio of complex:H₂O₂:cyclohexanol is 1:450:100, a complicated mixture containing mainly adipic acid was obtained. The composition of the product is under being studied.

Control experiments indicate that in the absence of the bis-quaternary phosphonium the oxidation of cyclohexanol and benzyl alcohol give cyclohexanone and benzaldehyde in rather low yields of 34.47% and 11%, respectively. The reaction was carried out in aqueous/organic biphasic system, but the peroxo Mo(VI) and W(VI) anion which take on catalytic ability are water soluble. Accordingly, the bis-quaternary phosphonium cations possessing lipophilic nature play an important role in the catalytic oxidation reaction because of its close combination with peroxo Mo(VI) and W(VI) anion.

3.4. Reaction catalytic cycle

Basing on the results of experiment, we proposed a possible catalytic cycle given in Scheme 1 for the biphasic oxidation. We inferred that close ion pair I, which parted between the aqueous phase and organic phase, was formed from the cation of bis-quaternary phosphonium (Q⁺) and the anion of peroxotungstate [W(O₂)]²⁻. The anion [W(O₂)]²⁻ in organic phase transferred its active oxygen to organic reactant, for instance, alcohol, and generated oxidant product, for instance, carbonyl compound. In the course of active oxygen



Scheme 1. Suggested catalytic cycle of the oxidation.

transfer, the deperoxotungstate [W(O)]²⁻ was generated. At the same meantime, the close ion pair II, which also parted between the aqueous phase and organic phase, was formed from Q⁺ and the anion of deperoxotungstate [W(O)]²⁻. In the aqueous phase, the H₂O₂ 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 entering the organic phase. Thereby, the catalytic cycle was finished. In this way, bis-quaternary phosphonium cation can catch peroxo Mo(VI) and W(VI) anion carrying active oxygen into organic phase where the oxidation reaction takes place effectively. Thus, the oxidation reactions get along successfully between two liquid phases and the yield of the products enhanced.

4. Conclusion

The result indicates the bis-quaternary phosphonium peroxomolybdates and peroxotungstates are effective catalyst in the oxidation of alcohol under the water–organic biphasic system. Although the exact mechanism of these bis-quaternary phosphonium peroxomolybdates and peroxotungstates catalyzing aqueous hydrogen peroxide solution to oxidize alcohol is still unclear, the catalytic system was carried out without organic solvent and halogen. Moreover, this catalytic oxidation system takes on the clean, safety and operationally simple characteristic, and the yields of the product are high, so the oxidation method meets the needs of contemporary green chemistry and is suitable for practical organic synthesis.

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