# Peroxo-tungsten complex catalysed synthesis of adipic acid and benzoic acid with hydrogen peroxide

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A new peroxo tungsten complex including N,N bidentate ligand was prepared and characterised, which catalysed $H_2O_2$ synthesis of adipic acid and benzoic acid in good yields without organic solvent and phase-transfer catalyst. The reaction is safe, clean and operational in the absence of acidic additives.

**Keywords:** peroxo tungsten complex, oxidation, hydrogen peroxide, catalysis, adipic acid, benzoic acid

Metal-catalysed oxidation of organic compounds with hydrogen peroxide is gaining increasing importance as a viable alternative to other, environmentally hazardous, oxidants. Tungsten and molybdenum compounds are widely applied to catalyse and oxidise a variety of organic substrates such as alkenes, alcohols, sulfides and amides with hydrogen peroxide, via homogeneous as well as heterogeneous routes.[1-11] Adipic acid and benzoic acid are important chemical materials, and are synthesised by various oxidants including $HNO_3$, $KMnO_4$, $CrO_3$ and $K_2O$, which are harmful to the environment. More recently, tungsten compounds such as $Na_2WO_4{\cdot}2H_2O$,[4,7,12] $H_2WO_4$,[8,13] $H_3PW_{12}O_{40}$,[14] $Q_4W_{10}O_{32}$[15] and $Q_3PW_4O_{24}$[16] (Q = quaternary ammonium) have been used to catalyse synthesis of adipic acid. In this water–organic biphase catalytic system, quaternary ammonium compounds and acidic complexes are usually co-catalysts, and act in the function of reaction phase-transfer. However, these co-catalysts are generally not environmentally benign. Pioneering works[5,8] indicated that the oxidation essentially occurred with tungsten peroxide species.

Catalytic systems using hydrogen peroxide oxidation of cyclohexene, cyclohexanol and cyclohexanone to adipic acid by tungstate/co-catalyst have been reported, but direct catalysis by peroxo tungsten complexes has received less attention. Based on the above summaries, we used, 10-phenanthrolinemonohydrate (Phen) as an N,N bidentate ligand and prepared the peroxo tungsten complex: $[WO(O_2)_2{\cdot}Phen]H_2O$ (**1**) (Fig.1), following Maiti *et al.*[17] but using Phen instead of 8-quinolinol.

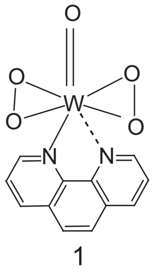
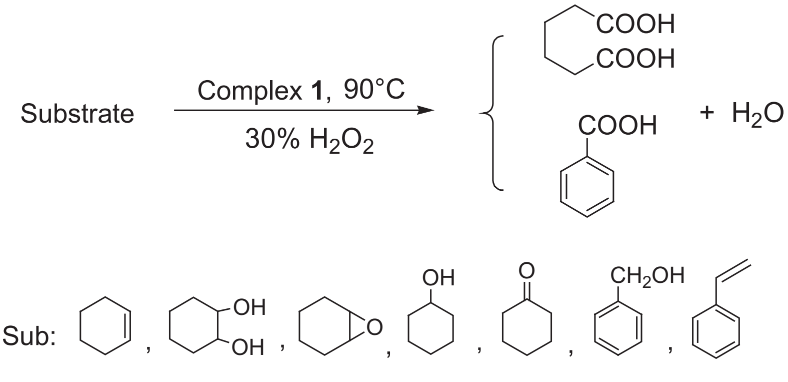


Fig. 1

So far as we are aware, there have been no literature reports on oxidation of cyclohexene, cyclohexanol, cyclohexanone, 2-cyclohexanediol, or cyclohexene oxide to adipic acid and oxidation of benzoic alcohol, or styrene to benzoic acid using $[WO(O_2)_2{\cdot}Phen]H_2O$ as catalyst without any co-catalyst. The catalytic system was operated at 90°C using aqueous 30 wt.% $H_2O_2$ without organic solvents, phase-transfer catalyst and halide (Scheme 1).

The oxidation of cyclohexanol, cyclohexanone, cyclohexene oxide, 1,2-cyclohexanediol, benzoic alcohol and styrene were then examined employing the optimised reaction conditions (Table 1). In the case of cyclohexene, the reaction resulted in 83.0% yield of adipic acid at 90°C refluxing for 20 h (entry 1). Under similar reaction conditions, cyclohexene oxide was oxidised to adipic acid with 85.9% yield. (entry 2). However, 1,2-cyclohexanediol gave less than 5.0% yield (entry 3). This may be attributed to the low solubility of complex **1** in aqueous 1,2-cyclohexanediol. The reaction system is thus heterogeneous, so the yield from 1,2-cyclohexanediol is low. In other reaction systems, complex **1** with the oleophilic ligand can be dissolved in the water-oil phase. Oxidation of cyclohexanol and cyclohexanone to adipic acid with lower yield was compared with oxidation of cyclohexene (entries 4 and 5). This procedure could also be applied to the oxidation of benzoic alcohol and styrene to benzoic acid (83.5% and



Scheme 1

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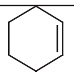
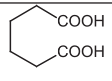
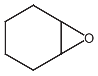
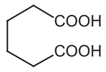
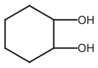
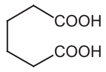
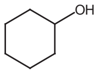
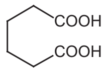
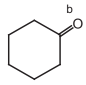
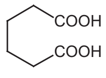
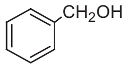
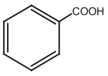
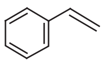
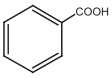
**Table 1** Oxidation of different substrates with hydrogen peroxide catalysed by $[WO(O_2)_2Phen]H_2O$

| Entry[a] | Substrate | Product | $H_2O_2$/mmol[c] | Time/h | Yield/%[d] | M.p./°C |
|---|---|---|---|---|---|---|
| 1 |  |  | 538 | 20 | 83.0 | 150–152 |
| 2 |  |  | 400 | 12 | 85.9 | 150–152 |
| 3 |  |  | 400 | 20 | <5 | – |
| 4 |  |  | 538 | 20 | 42.7 | 149–151 |
| 5 |  |  | 538 | 20 | 60.6 | 149–151 |
| 6 |  |  | 300 | 10 | 83.5 | 121–123 |
| 7 |  |  | 538 | 10 | 84.8 | 121–123 |

[a]Substrate: 100 mmol, catalyst: 0.9 mmol, Reaction temperature: 90°C.
[b]Cyclohexanone: 150 mmol.
[c]All reactions were performed in excess $H_2O_2$ over the stoicheometric amount required.
[d]The yield (based on substrate charged) referred to the isolated product.

84.8% yield). The melting points of adipic acid and benzoic acid products were 149–152°C and 121–123°C respectively (the reported results are 152°C and 122°C). The IR spectra of the product were identical to the standard spectra of adipic acid and benzoic acid. The results of chemical titration with standard solution of NaOH demonstrated the purity of the product was high (>99.5%).

In conclusion, a peroxo-tungsten complex with an N,N bidentate ligand was successfully synthesised, and could catalyse $H_2O_2$ and synthesise adipic acid and benzoic acid without organic solvent and phase-transfer catalyst. This catalytic system takes on clean, safe and operationally simple characteristics, and the yield of the product is satisfactory.

## Experimental

Complex **1** was synthesised from freshly precipitated $WO_3$ (6.0 mmol) in 30 wt.% $H_2O_2$ (10.0 ml) by stirring at room temperature. Addition of Phen (12.0 mmol) as an acetic acid solution (10.0 ml) to the above solution under stirring gave a white solid. The solid was filtered off, washed with water, 95% ethanol, diethyl ether and dried *in vacuo* at 30°C. Anal. Found, C, 31.4; H, 2.4; N, 6.0; W, 39.95; ($O_2^{2-}$), 13.90. Calc, C, 31.2; H, 2.2; N, 6.1; W, 39.8; ($O_2^{2-}$), 13.85. IR (selected bands, KBr disc; $cm^{-1}$) 955 [s; $\nu$ (M = O)], 885 [m; $\nu$ (O–O)], 621{s; $\nu_{sym}[M(O_2)]$}, 569{m; $\nu_{asym}[M(O_2)]$}. UV-vis ($CH_3CN$; nm) 228, 272.

*Oxidation Reaction Procedures:* In a 250 ml round-bottomed flask, the catalyst (0.9 mmol), substrate (100 mmol) and 30 wt.% $H_2O_2$ were introduced. The mixture was vigorously stirred at room temperature for 5 min and then heated and refluxed at 90°C with stirring for 20 h. After reaction was completed the reaction mixture was cooled at 5°C for 12 h. The resulting white precipitate was separated by filtration and washed with a saturated solution of standard adipic acid (5 ml portions) (entries 1 to 5) or benzoic acid (entries 6 and 7). The product was dried *in vacuuo* and determined by IR spectra, which accords with the IR spectra of standard adipic acid and benzoic acid, as well as the melting point.

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