Review Article

Journal of Atoms and Molecules
An International Online Journal
ISSN – 2277 – 1247

HYDROGEN PEROXIDE AS AN OXIDANT FOR ORGANIC REACTIONS

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Received on: 21-02-2013 Revised on: 26-02-2013 Accepted on: 28–02–2013

Introduction:

This review focuses on catalytic oxidation of organic compounds using hydrogen peroxide. Recent research has focused on the use of environmentally friendly oxidants such as oxygen [1,2] to replace stoichiometric toxic heavy metal oxidants such as dichromate and permanganates [3,4] in organic reactions. Hydrogen peroxide has in recent years become an increasingly important oxidant in chemical transformations involving organic reactions [5]. Hydrogen peroxide is a unique oxidant since it produces water as the only byproduct. In certain organic reactions, hydrogen peroxide is a better oxidant than oxygen since some oxygen/organic mixtures may spontaneously ignite [6]. Another merit of using hydrogen peroxide compared to other low cost oxidants such as sodium peroborate and many organic peroxy acids is its relatively high stability [5]. The limitation of using hydrogen peroxide as an oxidant in organic reactions is the unavoidable presence of water as the solvent of the commercial hydrogen peroxide and reduction products. A few reviews papers have been published on the use of oxygen in catalytic oxidation reactions [7-9]. However not much work has been reported in reviewing hydrogen peroxide mediated oxidation reactions. This review will discuss oxidations of amines, hydroxyamines, alcohols, ketones, sulphur and the various reaction mechanisms involved using hydrogen peroxide.

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Oxidation of alcohols

Various research groups have reported on both homogenous and heterogeneous catalysis of alcohols. Liquid phase alcohol oxidations proceed via a dehydrogenation mechanism [10-13] on surface of metals catalyst. The alcohol is initially dehydrogenated to form an alkoxide that is eventually dehydrogenated to form an aldehyde as illustrated by Equation 1.

$$RCH_2OH_{sol} \rightarrow RCH_2OH_{ads} \rightarrow RCHO_{ads} + 2H_{ads} \quad (1)$$

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Heterogeneous catalysis of alcohols

Bismuth modified platinum catalysts supported on carbon were reported [14-17] for the oxidation of hydroxymethylimidazoles (alcohols) to formylimidazoles (aldehydes) using hydrogen peroxide as illustrated in Fig. 1. Formylimidazoles are important in the preparation of pharmaceutical ingredients such as diuretics and antihypertensives. The reactions were carried out under alkaline conditions at mild reaction temperature (60-80ºC) and 100% selectivities towards formylimidazoles formation were attained. The results are shown in Table 1. Pt catalysts for liquid-phase oxidation reactions are sensitivity to deactivation caused by over-oxidation of the metal surface and by poisoning *via* the formation of strongly adsorbing side-products [18-20]. Addition of a second metal component such as Bi to Pt improves the catalytic activity and selectivity, and prolongs catalyst lifetime [18, 19, 21-24].

Campestrini et al., [25] reported the hydrogen peroxide oxidation of alcohols catalyzed by tetra-n-propylammonium perruthenata (TPAP) encapsulated in varying ratios of methyltrimethoxysylane (MTMS) and tetramethylorthosilicate (TMOS) sol gel. TPAP were found to be effective catalysts for oxidation of aromatic and aliphatic alcohols at room temperature (Table 2).

Metallosilicate (MO_x-SiO_2) xerogels were reported for the oxidation of alcohols to ketones [26] using 30% hydrogen peroxide. Oxidation of 1-phenylethanol produced various percentage yields of acetophenone over different metallosilicates: TiO_2-SiO_2 (2.1%), SeO_2-SiO_2 (3.4%), V_2O_5-SiO_2 (89.9%), MoO_3-SiO_2 (16.8%), WoO_3-SiO_2 (63.4%).

A new heterogeneous catalysis concept termed phase boundary catalysis (PBC) was reported for oxidizing hydrophobic alcohols over titanium metallosilicates [27]. Titanium (IV) oxides particles supported on alkyl modified silica particles were used as catalysts for the oxidation of alcohols using hydrogen peroxide at a boundary between a binary phase mixture of aqueous and organic interface. Various aromatic and cycling alkyl alcohols were oxidized with 30% H_2O_2 at 333 K under static conditions for 16 h in toluene (Table 3).

Various research groups have done extensive work on oxidation reactions of various organic substrates [28-35] over titanium silicalite 1 (TS-1). The mechanistic information of the oxidation of alcohols was further studied by van der Pol and van Hooff [36] using hydrogen peroxide. Catalytic reactions were carried out on 1-octanol, 2-octanol, 3-octanol, 2-heptanol, and 2-hexanol. These alcohols were exclusively oxidized to their corresponding aldehydes and ketones. The reactivity of different alcohols were shown to be influenced by the position of the hydroxyl group (γ-alcohols < α-alcohols << β-alcohols and the chain length, (C9 << C8 < C7 < C9).

Oxidation of various alcohols (Table 4) using hydrogen peroxide over iron exchanged montimorillonite-K10 catalyst was investigated [37]. Montimorillonites are dioctahedral phyllosilicates layered structures containing cationic exchange sites that are located between negatively charged silicate layers. Such a structure provides redox active metal ion centers within the interlayer space [38,39]. These metal centres act as useful catalysts in the presence of clay or zeolite.

A heterogenous polyoxometalate based mesoporous catalyst ($[ZnWZn_2(H_2O)_2(ZnW_9O_{34})_2]^{12-}$) for the oxidation of secondary alcohols was reported [40]. The results showed high conversions of aliphatic alcohols (92-100%) and 100% selectivity to the corresponding ketones**.**

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Homogenous catalysis of alcohols

Mechanism involving hydrogen peroxide oxygen

Catalytic oxidations of alcohols using hydrogen peroxide follow either the peroxometal pathway or the oxometal pathway. Fig. 2 [41] shows the two reaction mechanisms for alcohol oxidation. Peroxometal oxidations [42] typically involve early transition metal that have d^0 electronic configuration such as Re(VII), Ti(IV), Mo(VI), W(VI). There is no change in the oxidation state of the metal ion and no stoichiometric oxidation is observed in absence of hydrogen peroxide. Elements in the late series of transition metal elements and first row transition elements such as Cr(VI), Mn(V) and Os(VII) undergo oxometal [43] reaction pathway. Oxometal pathway involves change in metal ion oxidation state and stoichiometric oxidation is seen in the absence of hydrogen peroxide.

Alcohol oxidation reactions involving Mn catalysts

Berkessel and Sklorz [44] reported the oxidation of 2-pentanol to 2-pentanone (79% yield) with hydrogen peroxide using 0.03% manganese(II) acetate or sulphate catalyst. Manganese(III) Schiff base complex was used as a catalyst under mild and solvent free conditions [45] for the oxidation of alcohols to the ketones and carboxylic acids. The reaction products were easily isolated in good yields.

Alcohol oxidation reactions involving Ru catalysts

H_2O_2-$RuCl_3 \cdot H_2O$ phase transfer catalyst [46] was used for the selective oxidation of secondary alcohols to ketones (100% selectivity), primary benzylic alcohols to aldehydes (95-100% selectivity) and primary aliphatic alcohols to carboxylic acids (60-70% selectivity). The reactions were carried out at 80ºC and the role of the phase transfer was to extract H_2O_2 and $RuCl_3$ from the organic phase as well as maintaining the metallic catalyst in oxidized state. Table 5 summarizes results for the oxidation of various alcohols using 30% H_2O_2.

Alcohol oxidations involving Re catalysts

Alcohol oxidations with hydrogen peroxide can be catalyzed by methyltrioxorhenium (CH_3ReO_3, MTO) [47]. Hydrogen peroxide has been shown to oxidize alkenes [48,49], hydroxyamines [50] and halides [51,52] through addition of small amounts of MTO catalysts. The mechanism of such reactions involves the attack of the nucleophilic substrates on electron deficient peroxorhenium oxygen. In contrast, oxidation of alcohols proceeds by a different mechanism [53] as shown in Fig. 3. The oxidation reactions were done using 30% hydrogen peroxide catalyzed by MTO and HBr co-catalyst that enhances the reaction rate. The mechanism illustrates that an intermediate is formed in which the peroxorhenuium oxygen interacts with both the hydrogen and carbon atoms of the α-C-H bond. The intermediate can follow two parallel routes that generate the carbonyl.

A multicomponent system comprising MTO, hydrogen peroxide, 2,2,6,6 tetramethyl -1-piperidinyloxyl (TEMPO) and HBr in acetic acid was reported [54] to catalyze terminal alcohols to the corresponding alcohols with good yields and selectivity. The system was monitored on how reaction parameters (H_2O_2 concentration, reaction time and presence of TEMPO) could be adjusted to oxidize alcohols either selectively to aldehydes or to the corresponding carboxylic acids. The mechanism for TEMPO catalyzed oxidation is illustrated in Fig. 4 [55]. Epsenson and Zauche [56] observed that addition of HBr to the hydrogen peroxide MTO/HBr-catalyzed

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oxidation of alcohols accelerates by a factor of 1000 the conversion of alcohols to aldehydes and ketones. However this reaction failed to oxidize terminal alcohols such as benzyl alcohol. Addition of excess and stoichiometric quantities of hydrogen peroxide leads to generation of a mixture of aldehydes and carboxylic acids [56].

An efficient hydrogen peroxide oxidation of benzyl alcohols to aldehydes using TEMPO/HBr/H_2O_2 in ionic liquid [bmim]PF_5 was reported [57]. Electron deficient and neutral benzyl alcohols gave good selectivities and conversions (80%) whereas electron rich substituted benzyl alcohols gave low aldehyde yields due to side reactions. The reactions were performed under mild (50ºC) temperatures. The ether insoluble acetamido-TEMPO could be recycled and reused.

Alcohol oxidations involving V catalysts

Vanadium phosphorus oxide is an effective catalyst for the liquid phase oxidation of alcohols using hydrogen peroxide and acetonitrile at 65ºC under nitrogen atmosphere [58]. The oxidation mechanism was believed to involve a reversible redox cycle of V^{4+} and V^{5+} active species. The result for oxidation of hydrogen peroxide oxidation of various alcohols is shown in Table 6.

Alcohol oxidations involving Fe catalysts

Alcohols and aldehydes can be oxidized by Fenton's reagent which is a system of Fe^{2+} and hydrogen peroxide. The reaction proceeds via a free radical reaction mechanism as illustrated by equations 2-6 [59-61].

Chain initiation:

$$HO - OH + Fe^{2+} \rightarrow Fe^{3+} + \dot{O}H + OH^{-} \quad (2)$$

Chain propagation:

$$RH_2OH + \dot{O}H \rightarrow R - \dot{C}HOH + H - \dot{O}H \ (reversible) \quad (3)$$

$$R - CHOH + HO - OH \rightarrow \dot{O}H + RCHO + H_2O \quad (4)$$

Chain termination at low alcohol concentration:

$$Fe^{2+} + \dot{O}H \rightarrow Fe^{3+} + OH^{-} \quad (5)$$

Chain termination at high alcohol concentrations:

$$2R - CHOH \rightarrow R - CHO + R - CH_2OH \ (disproportionation) \quad (6)$$

Fenton's reagent was successful applied in the oxidation of phenol [62]. The rate of oxidizing phenol was found to be dependent on the concentration of hydrogen peroxide up to a limiting value above which the oxidation remained constant. Malik and Saha [63] reported the oxidation of phenolic organic dyes using Fenton's reagent. The dyes were decomposed in a two stage process. The rate of decomposition of the dyes was depended upon pH, temperature, hydrogen peroxide concentration and reaction time.

Benzylic alcohols and secondary alcohols were selectively oxidized with hydrogen peroxide using $FeBr_3$ catalyst [64]. The secondary alcohols were selectively oxidized to ketones in the presence of primary alcohols. The reactions were carried out at room temperature in acetonitrile or under

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solvent free conditions. Table 7 shows the results for the oxidation of various alcohols.

Alcohol oxidations involving W catalysts

Sato *et al* [65-67] reported the selective oxidation of various substituted benzyl alcohols to benzaldehydes or benzoic acids using 30% hydrogen peroxide under halide free biphasic conditions. A system comprising Na_2WO_4 catalyst, toluene solvent and a phase transfer catalyst methyltrioctylammonium gave 80-91% benzaldehydes yields. Various ring substituted benzyl alcohols were directly oxidized to carboxylic acids using 2.5-5 equivalent hydrogen peroxide. The mechanism for alcohol oxidation is illustrated in Fig. 5. Na_2WO_4 and a phase transfer catalyst were also used in the oxidation 1-octanol, 2-octanol, cylclohexanol and benzyl alcohol under phase transfer conditions using hydrogen peroxide [68]. The carbonyl yields were found to be between 85 and 97%. Complete substrate conversion was obtained with 2-6 fold hydrogen peroxide concentration. Excessive amounts of hydrogen peroxide leads to formation of small amounts of benzoic acid.

A water soluble polyoxometalate, $WZnZn_2(H_2O)_2(ZnW_9O_{34})_2$ catalyst was reported [69] for the hydrogen peroxide oxidation of alcohols without addition of an organic solvent. Liquid secondary alcohols (cyclohexanol, 2-pentanol, 2-octanol, 1-phenylethanol) were selectively oxidized to ketones (100% selectivity). However, primary alcohol such as benzyl alcohol and 1-pentanol were oxidized to the carboxylic acids. Addition of TEMPO partially inhibits carboxylic acid formation as some aldehydes were formed.

A catalyst imidazodium-based phosphotungstate [70] was used in the oxidation of alcohols with hydrogen peroxide in ionic liquid [bmim][BF_4]. Compared to quaternary ammonium terakis(diperoxotungsto)phosphate catalysts [71] these homogenous catalysts system offers a low degree of consumption of the solvent, ready product separation and easy system recycle without much decrease in product yield. Excellent selectivities (100%) and good yields (>78%) of cycling and aromatic ketones were obtained. Yields of primary alcohols to aldehydes were good but the conversions were lower than for secondary alcohols under the same reaction conditions. For instance, benzyl alcohol, produced 78% benzaldehyde and minute amounts of benzoic acid in 8 h.

Catalytic oxidation of carbohydrates

The C6-hydroxymethyl group was completely oxidized to carboxylic using H_2O_2/MTO/HBr system [56]. The proposed reaction mechanism is shown in Fig. 6. The formation of hypobromite in the presence of excess hydrogen peroxide ensured that no aldehyde was formed but only the desired carboxylic acid.

Hydrogen peroxide mediated oxidation of starch under basis and acid conditions were reported using tungsten, copper and iron catalysts [72]. Carbonyl groups (6.6 per 100 glucose units) and carboxyl groups (1.4 per 100 glucose units) were introduced. Starch conversion was lower in alkaline medium (90%) than in acid (99%).

Catalytic oxidation of aldehydes

Acid catalyzed oxidation of aldehydes to carboxylic acids in acidic quaternary salt ($[CH_3(n\text{-}C_8H_{17})_3NSO_4)$, $QHSO_4$ was reported [73]. The reaction was carried out in 30% H_2O_2 at 90ºC. The results obtained are shown in Table 8. The reaction occurs via the formation of perhydrate intermediate (Fig. 7). The acidic quaternary salt assists the addition of hydrogen peroxide to aldehydes in organic layer and facilitates the elimination of water

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from the tetrahedral intermediate via a Baeyer-Villiger oxidation [74, 75].

Aliphatic aldehydes and aromatic aldehydes were oxidized to carboxylic acids with 30% hydrogen peroxide over selenium (IV) oxide catalysts [76]. High percentage yield of aromatic carboxylic acid (73-96%) and aliphatic carboxylic acid (>80%) were obtained.

Catalytic oxidation of sulfides

Sulphides can be oxidized to sulfoxides or sulfones depending on reactions conditions. Oxidation of sulfides to sulfones can be attained more easily than selective oxidation of sulfides to sulfoxides [77-79]. This can be explained in terms of relatively easy of overoxidation of sulfoxides to sulfones. MTO has been reported to be an execellent catalyst for the oxidation of sulfides to sulfoxides or sulfones at room temperature using hydrogen peroxide [80]. Selective oxidation of sulfides was attained by adjusting the concentration of oxidant and MTO. For instance the use of 2.2 M H_2O_2 and 2 mol% MTO resulted in overoxidation of sulfoxide to sulfones whereas 0.5 M H_2O_2 and 1 mol% MTO yielded 99% diphenyl sulfoxide and 1% diphenyl sulfones at 99% diphenyl sulphide conversion (Fig. 8). Functional groups in the side chain of the sulfide such as carbon-carbon double bonds were not oxidised.

Various tungsten catalysts [77-87] have been reported for the hydrogen peroxide oxidation of sulfides. These catalytic systems make use of chlorohydrocarbons solvents that have harmful effects to human. Sato *et al.*, [86] reported the use of Na_2WO_4 catalyst in the organic solvent and halogen free oxidation of sulfides using 30% H_2O_2. A quartenary salt was used as a PTC in the absence of an organic solvent and the reaction was carried out at 25ºC for 2 h. Aliphatic and aromatic sulfides were oxidized to sulfoxides or sulfones in excellent yields (90-99%). The proposed catalytic cycle (Fig. 9) shows that the acidic hydrogen sulfate ion generates the bis(peroxo)-tungsten mono-anion and the lipoliphic quaternary ammonium ion transports the hydrogen peroxide to the organic phase. The mono(peroxo)tungsten ion is deoxidized to the bis(peroxo) species either in the organic or aqueous phase.

Bicarbonate catalyzed oxidation of sulfides to sulfones or sulfoxides were investigated [87]. The reactions were carried out at 25ºC in 2 M aqueous H_2O_2 in different alcohol/water solutions. The bicarbonate ions were effective catalysts for such oxidation reactions. Kinetic and spectroscopic data shows that during the catalytic reaction the peroxymonocarbonate ion (HCO_4^-) is formed as the oxidant (Equations 7-11).

$$HCO_3^- + H_2O_2 \rightarrow HCO_4^- + H_2O \quad (7)$$

$$HCO_3^- + R''OH \rightarrow R''CO_3^- + H_2O \quad (8)$$

$$HCO_4^- + RSR' \rightarrow RS(O)R' + HCO_3^- \quad (9)$$

$$HCO_4^- + RSR' + H_2O_2 \rightarrow RS(O)R' + HCO_3^- + H_2O_2 \quad (10)$$

$$RS(O)R' + [O] \rightarrow RS(O)_2 R' \quad (11)$$

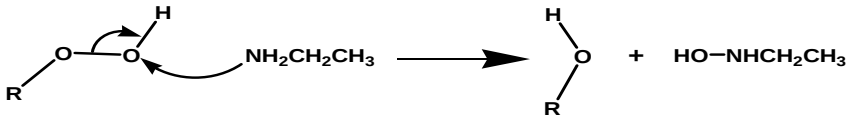
A two phase system comprising an aqueous solution of neutral Mo(VI) peroxo complexes (Na_2MoO_4) was transferred by lipophilic monodentate neutral ligand in dichloroethane for the oxidation of sulfide using H_2O_2. Excellent sulfoxide yields (87-100%) were recorded [88]. Effective hydrogen peroxide oxidations of sulfide using catalysts such as CH_3ReO_3 [89] and 2-$NO_2C_6H_4SeO_2H$ [90]

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dissolved in chlorohydrocarbon solvents were reported.

Catalytic oxidation of amines

The generally accepted reaction mechanism of the reaction of hydrogen peroxide with amines [91] involves the nucleophilic attack on distal oxygen with a direct S_N2 displacement of the β-peroxy oxygen (Equation 12).



(12)

Amine N-oxides are industrial important oxidants [92-95] that are prepared by a slow reaction of hydrogen peroxide oxidation of tertiary amines [96]. Current research has reported more efficient catalytic hydrogen peroxide oxidations of aromatic N-heterocyclic compounds to the corresponding N-oxides using manganese porphyrin [93] and methyltrioxorhenium(VII) [98,99].

Flavin catalysts have been used in a highly effective H_2O_2 oxidation of tertiary amines [100]. Several aliphatic amines were oxidized to their corresponding N-oxides in good yields (>85%) and short reaction times (25-60 min). The proposed catalytic cycle for the oxidation of tertiary amines to N-oxides (Fig. 10) has shown that both H_2O_2 and O_2 are essential for the oxidation.

Catalytic oxidation of 1,2-diols

Hydrogen peroxide mediated oxidative cleavage of water soluble 1,2 diols to carboxylic acids was reported using minute amounts of catalytic tungstate (WO_4^{2-}), arsetate (AsO_4^{3-}) and phosphate (PO_4^{3-}) ions [101]. The oxidations were effectively performed under acidic conditions (pH 2) at 90ºC. Excellent yields of carboxylic acids were obtained (Table 9).

Various research groups have reported the oxidation of 1,2-diols to 1,2-diketones using *N*-bromosuccinimide [102], O_2-$Co(acac)_3$-*N*-hydroxyphthalimide [103]. However, the major drawbacks of these methods are use of expensive reagents, long reaction times and strenuous experimental conditions and low product yield. Jain et al [104] reported an eco-friendly methyltrioxorhenium oxidation of 1,2-diol to their corresponding 1,2-diketones using 30% hydrogen peroxide. Hydrobenzoins gave higher yields (80-97%) than aliphatic diols (70-75%). A water trapping agent $MgSO_4$ was added to the reaction mixture to improve the yield of ketones since the reaction that was selective to ketones is affected by moisture.

Vic diols were successful oxidized to corresponding 1,2-diketones in good yields (80-81%) using $H_2O_{2(aq)}$ in the presence of peroxotungstophosphate catalyst [105].

Conclusion

The oxidation of various organic compounds using hydrogen peroxide has been reviewed. High percentage yields and selectivities were obtained for most of the reactions. Catalytic oxidation of organic compounds using hydrogen peroxide plays an essential role in the formation of important industrial compounds. A great number of heterogeneous and homogenous catalysts were discussed for the environmentally friendly oxidation of organic compounds using hydrogen peroxide. The potential of hydrogen peroxide in the oxidation of various organic functional groups opens up opportunities to develop new and novel catalysts that can be exploited in industrial applications. The use of gold in hydrogen peroxide mediated oxidations would be one area that requires further evaluation.

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Tables

Table 1. Hyrogen peroxide mediated oxidation of hydroxymethylimidazoles over carbon supported Pt-Bi catalysts

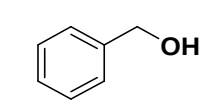
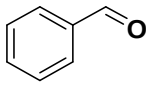
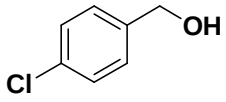
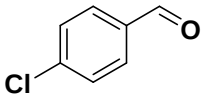
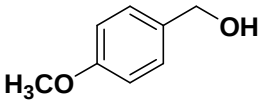
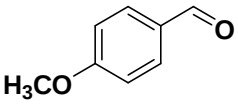
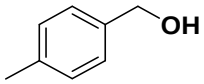
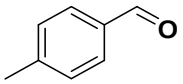
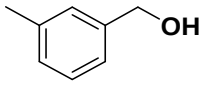
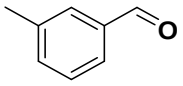
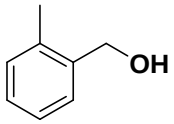
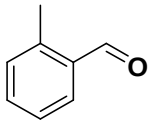
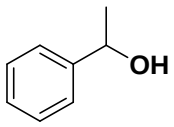
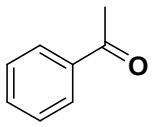
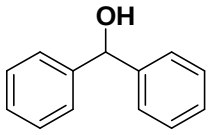
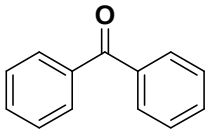
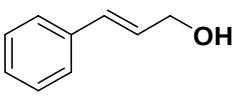
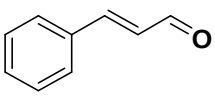
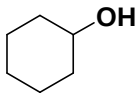
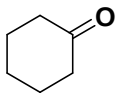
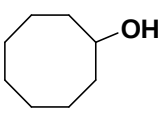
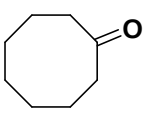
Catalyst	Alcohol	Aldehyde	Yield (%)	Conditions	Ref.
5%Pt-5%Bi/C	2-n-butyl-4-chloro-5-hydroxymethylimidazole	2-n-butyl-4-chloro-5-formylimidazole	67.3	20% H_2O_2, 60°C, 60 min	14,17
5%Pt-5%Bi/C	2-n-butyl-4-chloro-5-hydroxymethylimidazole	2-n-butyl4-chloro-5-formylimidazole	93.5	20% H_2O_2, 60°C, 90 min	14
5%Pt-5%Bi/C	2-n-butyl-5-hydroxymethylimidazole	2-n-butyl-5-formylimidazole	88.2	15.7% H_2O_2, 60°C, 60 min	15
5%Pt-5%Bi/C	2-n-butyl-5-hydroxymethylimidazole	2-n-butyl-5-formylimidazole	100	15.7% H_2O_2, 60°C, 60 min	15
5%Pt-5%Bi/C	4-[(2-butyl-5-hydroxymethyl-1-H-imidazol-1-yl) methyl benzoic acid]	4-[(2-butyl-5-formyl-1-H-imidazol-1-yl) methyl benzoic acid]	70	20% H_2O_2, 60°C, 60 min	16

Table 2. Alcohol oxidations with H_2O_2 catalyzed by TPAP encapsulated pure silica at room temperature

Substrate	Alcohol conversion	Aldehyde selectivity (%)	Carboxylic acid selectivity (%)
Benzyl alcohol	94.3	100.0	0.0
1-Phenylethanol	63.3	100.0	0.0
1-Octanol	71.6	41.7	29.9
2-Octanol	58.9	100	0.0
Geraniol	62.9	40.5	59.5
Furfuryl alcohol	40.0	28.2	71.8
Borneol	20.0	100.0	0.0

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Table 3. Oxidation of aromatic and cyclic alkyl alcohols over TiO_2 supported on amphiphilic silica particles, using 30% H_2O_2

Substrate	Carbonyl product	Carbonyl product yield (%)	Carbonyl product selective (%)
		16.1	97
		16.6	92
		15.0	74
		22.6	80
		18.5	92
		14.3	99
		10.6	100
		11.3	100
		8.0	35
		6.3	100
		14.8	88

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Table 4 Oxidation of alcohols over Fe^{3+}/montmorillonite-K10 using hydrogen peroxide and acetonitrile

Substrate	**Product**	**Conversion (%)**	**Selectivity (%)**
1-pentanol	1-pentanal	12	100
2-pentanol	2-pentanone	25	100
cyclopentanol	cyclopentanone	42	92
3-pentanol	3-pentanone	30	100
1-hexanol	1-hexanal	11	100
2-hexanol	2-hexanone	31	100
3-hexanol	3-hexanone	37	100
cyclohexanol	cyclohexanone	35	100
1-methyl cyclohexanol	1-methyl cyclohexanone	5	100
2-methyl cyclohexanol	2-methyl cyclohexanone	38	100
3-methyl cyclohexanol	3-methyl cyclohexanone	25	100
4-methyl cyclohexanol	4-methyl cyclohexanone	37	100
Cinnamyl alcohol	cinnamaldehyde	95	20
1-phenyl ethanol	acetophenone	86	95
2-phenyl ethanol	Phenyl acetadehyde	39	40
benzyl alcohol	benzaldehyde	>95	32
3-chlorobenzyl alcohol	3-chloro benzaldehyde	>95	5

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Table 5. Hydrogen peroxide oxidation of alcohols using $RuCl_3$ catalyst under phase transfer conditions

Substrate	Main product	Conversion (%)	Sel. to main product (%)
cyclohexanol	cyclohexanone	90	100
2-octanol	2-octanone	82	100
Sec-phenethyl alcohol	acetophenone	90	100
Benzyl alcohol	benzalaldehyde	91	95
p-methyl benzyl alcohol	p-methylbenzadehyde	86	100
p-nitrobenzyl alcohol	p-nitrobenzaldehyde	80	100
p-bromobenzyl alcohol	p-bromobenzaldehyde	45	100
1-decanol	1-decanoic acid	87	66
1-octanol	1-octanoic acid	85	68
1-heptanol	1-heptanoic	89	73
1-hexanol	1-hexanoic acid	85	67

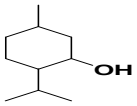
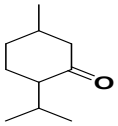
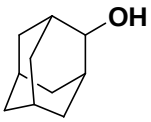
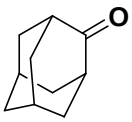
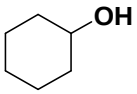
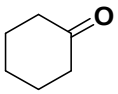
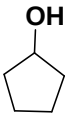
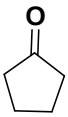
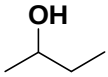
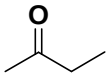
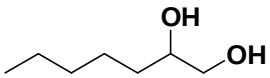
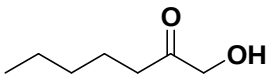
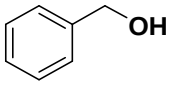
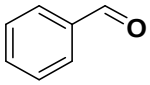
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Table 6. Hydrogen peroxide oxidation of various alcohols using VPO catalysts

Alcohol	Product	Conversion (%)	Selectivity (%)
1-pentanol	1-pentanal	6	100
2-pentanol	2-pentanone	33	100
3-pentanol	3-pentanone	38	100
1-hexanol	1-hexanal	7	100
2-hexanol	2-hexanone	59	100
3-hexanol	3-hexanone	52	100
cyclohexanol	cyclohexanone	44	100
2-methyl cyclohexanol	2-methyl cyclohexanone	39	100
3-methyl cyclohexanol	3-methyl cyclohexanone	32	100
4-methyl cyclohexanol	4-methyl cyclohexanone	40	100
4-t-butyl cyclohexanol	4-t-butyl cyclohexanone	40	100
cycloheptanol	cycloheptanone	61	100
2-octanol	2-octanone	23	100
benzhydrol	benzophenone	52	100
Benzyl alcohol	benzaldehyde	66	78
1-phenyl ethanol	acetophenone	77	100
2-phenyl ethanol	phenyl benzaldehyde	10	100

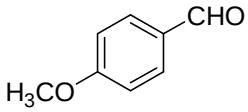
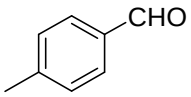
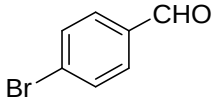
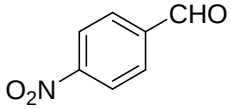
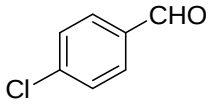
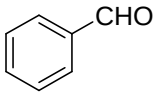
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Table 7. Oxidation of alcohols without solvents and in acetonitrile

Substrate	Product	Solvent	Yield (%)
		Acetonitrile	92
		none	18
		Acetonitrile	87
		none	25
		Acetonitrile	83
		none	90
		Acetonitrile	89
		none	92
		Acetonitrile	94
		none	95
		Acetonitrile	82
		none	89
		Acetonitrile	70
		none	91

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Table 8. Oxidation of aldehydes catalyzed by acidic quaternary salt

Aldehyde	**% Yield of caboxylic acid**
$C_6H_5(CH_2)_2CHO$	77
n-$C_7H_{35}CHO$	85
p-$[CH_3CH(OH)]C_6H_4CHO$	79
n-$C_4H_9CH(C_2H_5)CHO$	65
$(CH_3)_3CCHO$	40
$C_6H_5CH(CH_3)CHO$	17
	9
	41
	78
	88
	76
	85
$HO(CH_2)_{10}CHO$	75
$CH_2CH(CH)_5CHO$	85

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Table 9. Hydrogen peroxide mediated oxidative cleavage of 1,2-diols to carboxylic acids using WO_4^{2-} or PO_4^{3-} catalysts

Substrate	Product	Yield (%)
Trans-1,2-cyclo pentanediol	Glutaric acid	96
Cis-1,2-cyclo-hexanediol	Adipic acid	92
Trans-1,2-cyclo-hexanediol	Adipic acid	94
Trans-1,2-cyclo-heptanediol	Pimelic acid	87
Trans-1-methyl-1,2-cyclohexanediol	6-oxoheptanoic acid	93
1-phenyl-1,2-ethanediol	Benzoic acid	87
1,2-hexanediol	Valeric acid	92
2,3-butanediol	Acetic acid	87
1,2-propane-diol	Acetic acid	90
3-methyl-2,3-pentanediol	Acetic acid	90

Figures

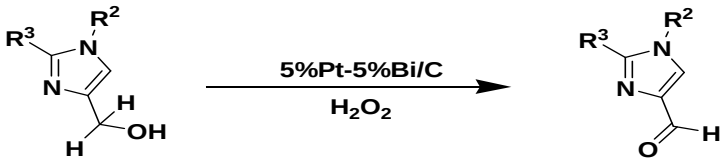


Figure 1. Oxidation of hydroxymethylinidazole.

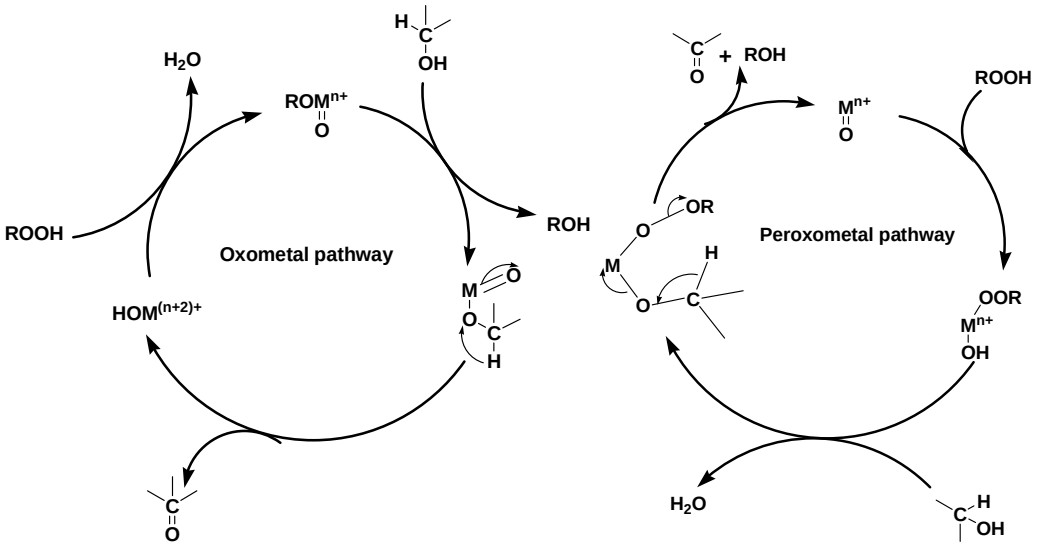


Figure 2. Oxometal and peroxometal reaction pathways [41].

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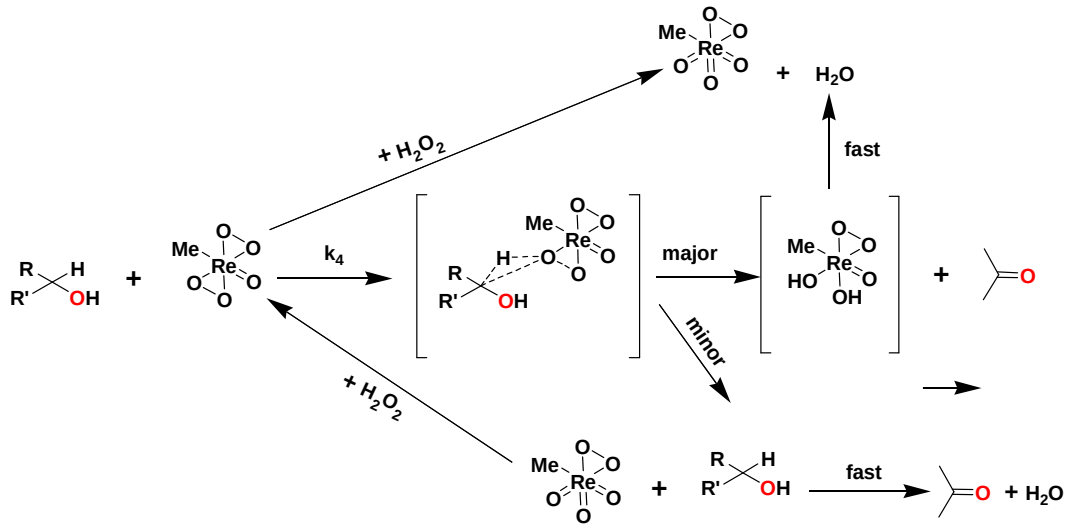


Figure 3. Reaction mechanism for the hydrogen peroxide oxidation of alcohols using MTO catalysts [53].

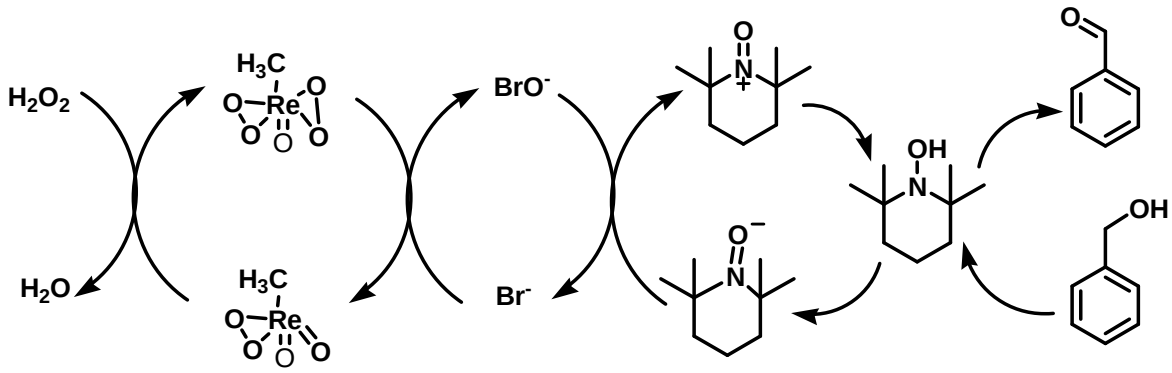


Figure 4. H_2O_2 mediated oxidation of alcohols with MTO/HBr/TEMPO catalyst [55].

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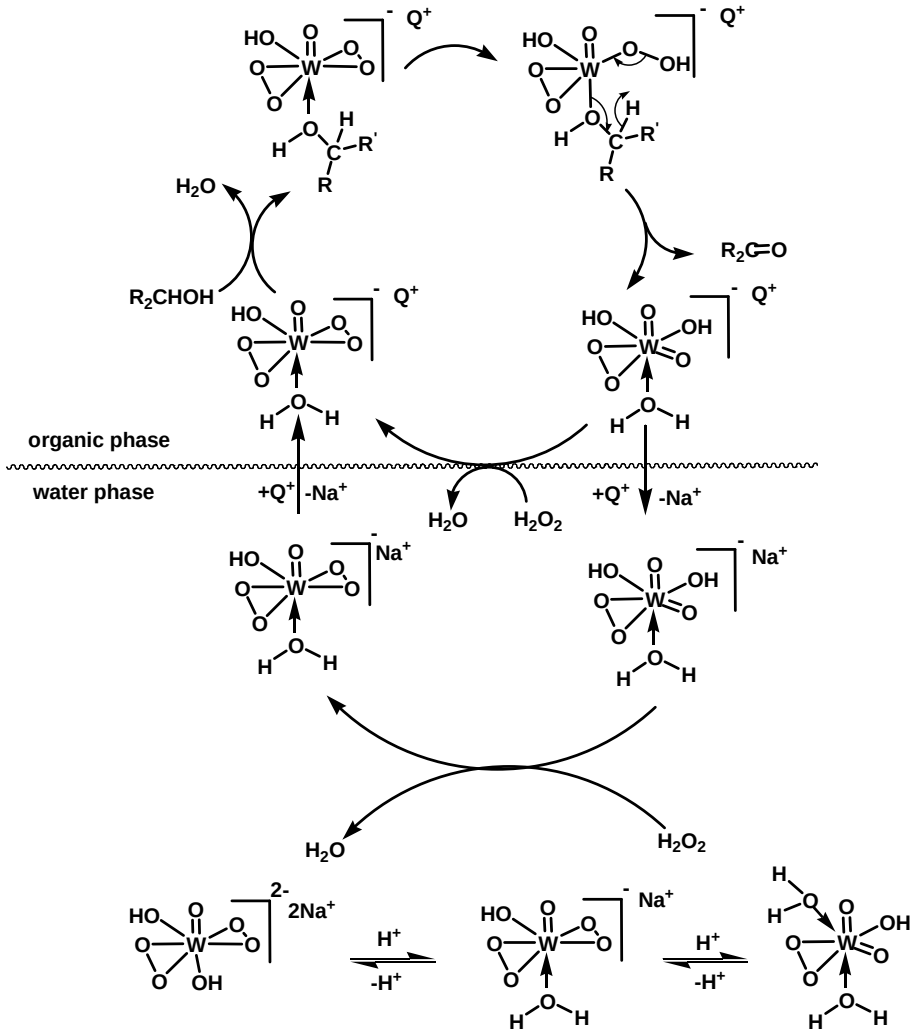


Figure 5. Mechanism of alcohol oxidation in WO_4 using PTC (Q- quaternary salt) [66].

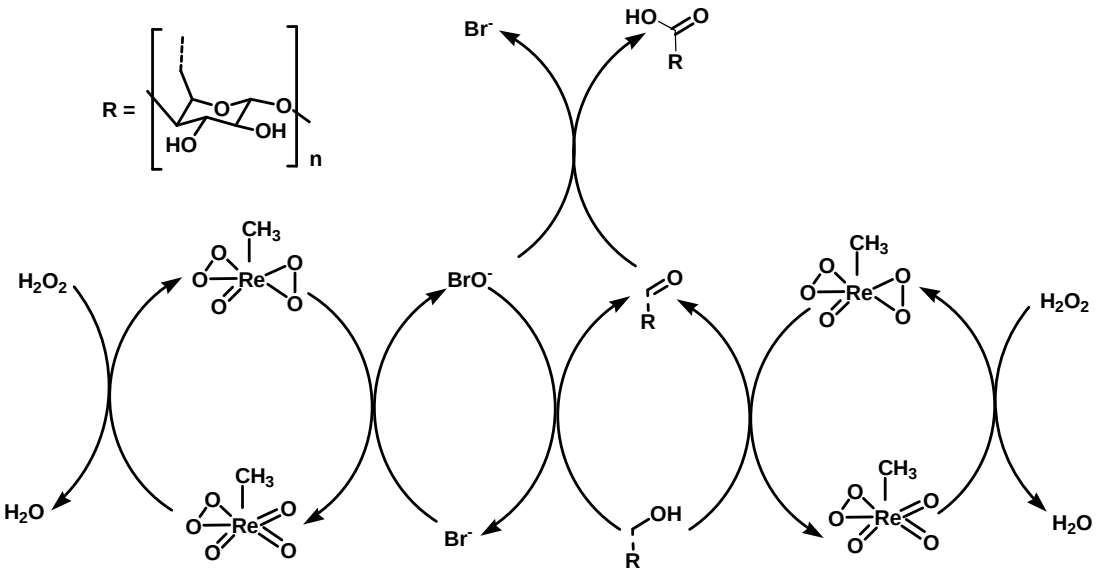


Figure 6. Mechanism for H_2O_2 mediated oxidation of starch [56].

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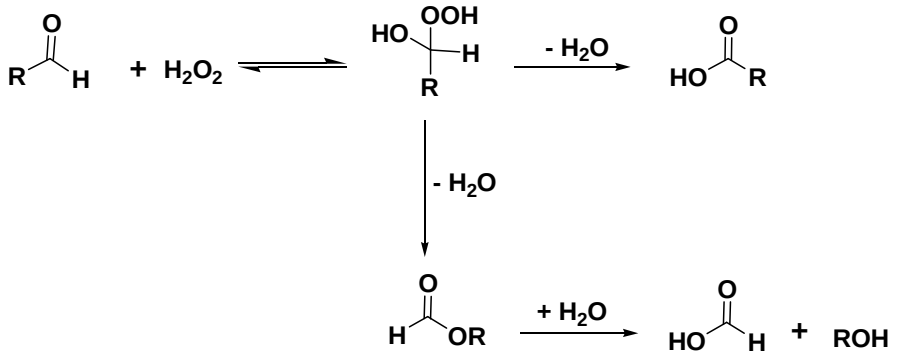


Figure 7. Reaction mechanism for oxidation of aldehydes to carboxylic acid [73].

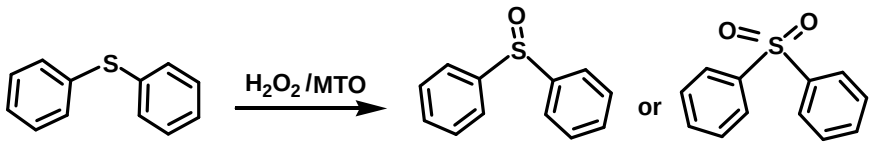


Figure 8. Hydrogen peroxide mediated oxidation of diphenyl sulphide [80].

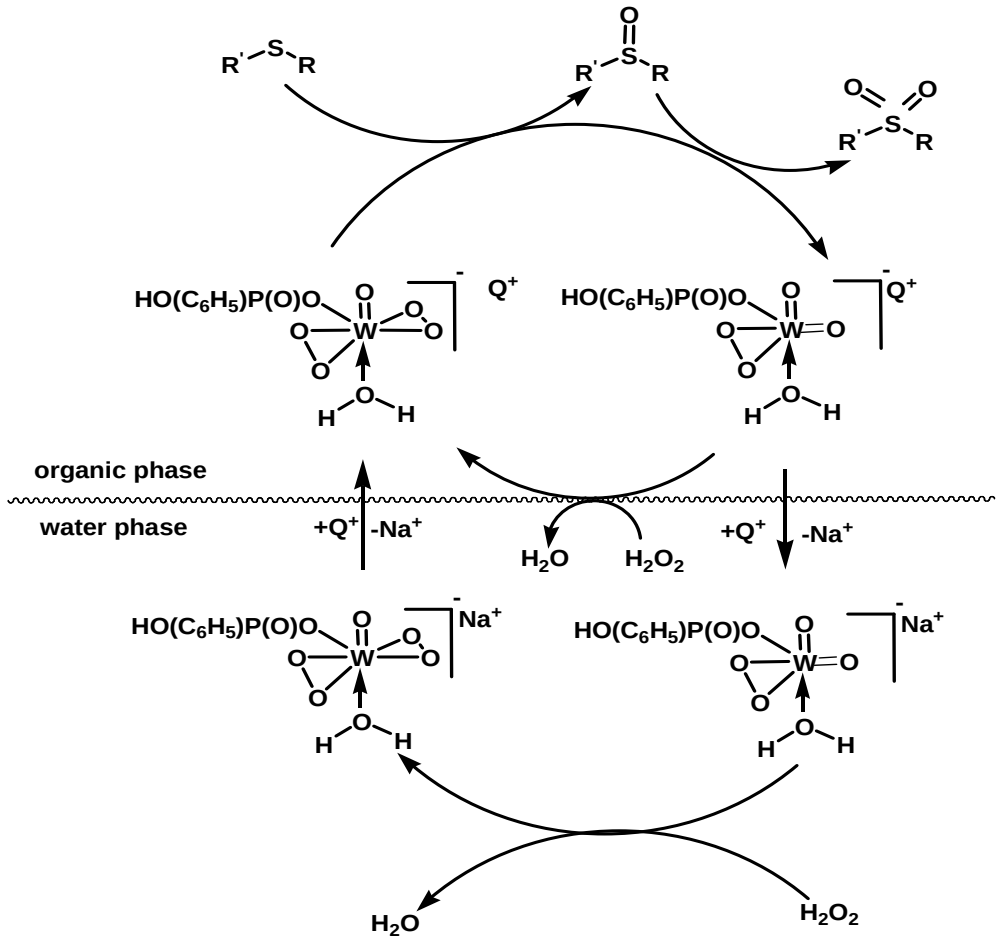


Figure 9. Catalytic cycle for solvent free oxidation of sulfides using tungsten catalyst (Q-quaternary salt) [82].

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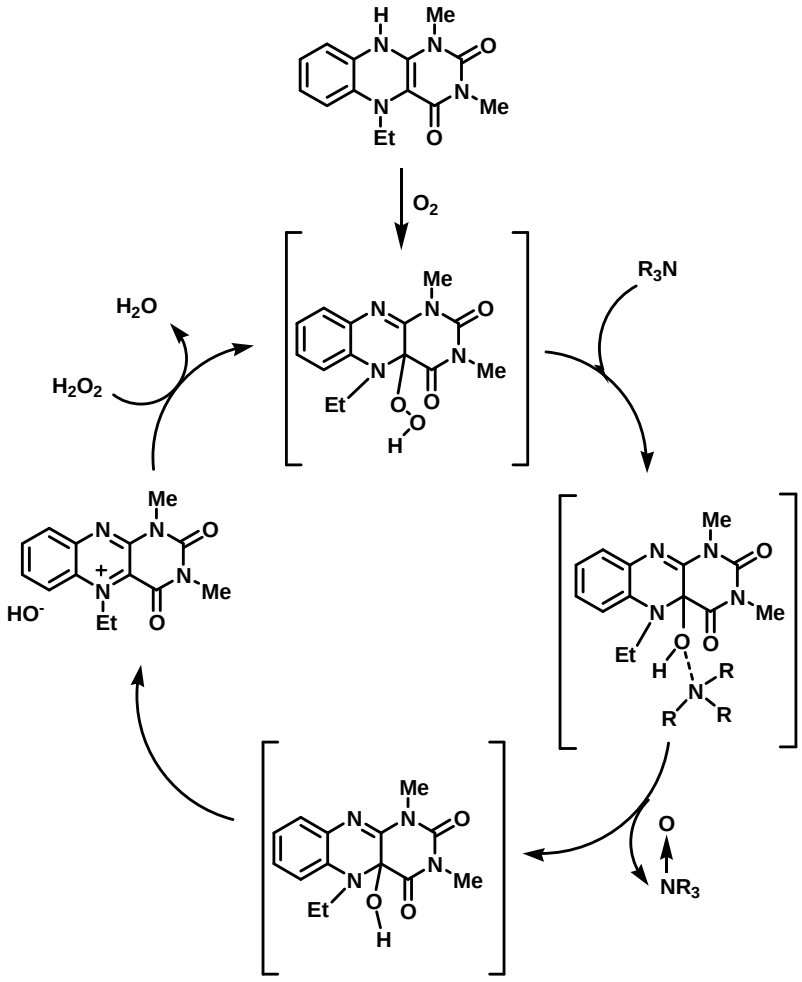


Figure 10. Hydrogen peroxide mediated oxidation of tertiary amines using flavin catalyst [100].

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