

NEW ELECTROCATALYTIC METHOD FOR STEREO-SELECTIVE OXIDATIONS

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ABSTRACT

A metal catalyst-mediated selective transfer of an oxygen atom from a cheap, electrochemically generated, single oxygen donor such as tert-butyl hydroperoxide to substrate has been described. (\pm) Isborneol is stereospecifically oxidized to (+) camphor.

Key Words: Electrocatalyst, stereo selective oxidation

INTRODUCTION

Catalytic processes enjoy several important advantages compared to their non-catalytic counterparts. These are: (i) they proceed under milder conditions and are more energy efficient (ii) they are selective, and provide for an optimal utilisation of raw materials (iii) the steps involved are fewer and (iv) they produce less amount of inorganic effluents.

The emphasis in organic synthesis today is placed firmly on selectivity. Often organic chemists striving to synthesize organic molecules of ever-increasing complexity, are continually seeking new methods for achieving *chemo, regio and stereoselectivity*. The problem of selectivity and the need for selective catalysis is nowhere more apparent than in oxidation processes [1].

The basic concept involved in the reaction is that a metal catalyst mediates the selective transfer of an oxygen atom from an electrochemically generated tertbutyl hydroperoxide (TBHP) which is prepared from readily available tert-butyl alcohol. In the absence of the metal catalyst there is no reaction between the oxidant and the substrate. Alkyl hydroperoxides (ROOH) and dialkyl peroxide (ROOR) are derivatives of hydrogen peroxide (H₂O₂). Their thermal stability generally increases in the order primary < secondary < tertiary alkyl. The TBHP and di-t-butyl peroxide (DTBP) are two of the most stable organic peroxides.

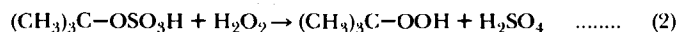
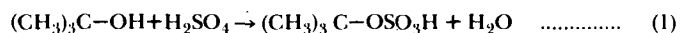
The TBHP was first prepared in 1938 [2]. In the late sixties it was discovered that propylene could be selectively epoxidized by TBHP in the presence of a homogeneous molybdenum catalyst [3,4]. The following are the advantages of TBHP to other more wellknown oxidants such as H₂O₂ and peracetic acid [5]:

- i) TBHP has a high thermal stability in dilute organic solutions. e.g. 0.2M solution of TBHP in benzene has a half-life of 520 hours at 130°C.
- ii) TBHP is less sensitive to contamination by metals than H₂O₂ or peracetic acid and is consequently safer to handle.
- iii) The main advantage of TBHP is its selectivity and is unreactive to most organic compounds in the absence of a metal catalyst.
- iv) It is readily soluble in hydrocarbon solvents.
- v) Oxidations are carried out under neutral conditions.
- vi) The decomposition is t-butanol which can readily be removed by distillation (boiling point 83°C).

EXPERIMENTAL

Chemical synthesis of TBHP

The chemical procedure [6,7] for the synthesis of TBHP, comprises of (a) preparing t-butyl hydrogen sulphate in situ from equimolar quantities of a t-butanol and 70% sulphuric acid and (b) addition of 30% hydrogen peroxide to this. The reaction can be represented as



Electrochemical synthesis of TBHP

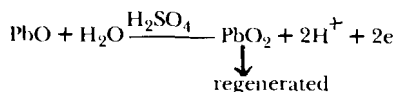
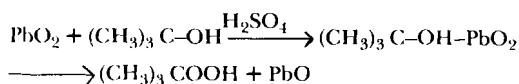
No one has so far reported the electrochemical synthesis of TBHP or any other alkyl hydroperoxide. The advantages of electrochemically generating TBHP are manifold but the main ones are:

- i) In situ generation of TBHP in an electrochemical reactor where this reacts directly with the organic substrate in presence of suitable transition metal cation.
- ii) The conditions for electrochemical generation for TBHP are much milder than chemical method.
- iii) The possibility of any explosion is completely ruled out due to milder conditions and simultaneous utilization of TBHP generated.
- iv) Storage problem is avoided.

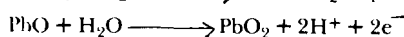
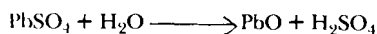
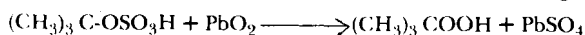
The following method has been worked out:

From the equimolar mixture of 10N to 15N H₂SO₄ and t-butanol, the t-butyl hydrogen sulphate was prepared and the same in an appropriate solvent like t-butanol, methylene chloride or benzene containing supporting salts like tetraalkylammonium sulphate was electrolysed at lead dioxide anode; the cathode was of lead wrapped with blue asbestos. For preparing PbO₂ anode, platinum electrodes were polarised at 25 mA cm⁻², for 1 hr at 50–60°C in magnetically stirred bath of 100 g dm⁻³ Pb(NO₃)₂ and 2 g dm⁻³ concentrated nitric acid. Alternatively, the lead sheet was anodised for 1 hr in 2N H₂SO₄ at a current density of 10 mA cm⁻² at room temperature.

The PbO₂ is known to be a strong chemical oxidant, especially in acidic solutions. The lead dioxide anode as an oxygen electrode or as a synthesis anode is commonly regarded as inert electrode material. The t-butyl hydrogen sulphate in the bulk gets adsorbed at the electrode surface and gets oxidised to hydroperoxide and sulphuric acid is liberated, which again helps in regenerating the oxidised surface at the anode in the form of lead dioxide.



Alternatively, when alkyl hydrogen sulphate is taken as starting material, the reaction in all probability proceeds in the following manner:



Stereospecific oxidation

The TBHP generated at the electrode surface is able to bring about the *stereo-specific oxidation* of (\pm) isborneol to (+) *camphor*. The TBHP can be generated electrochemically at lead dioxide anode which can be used for the continued stereospecific oxidation of organic compounds in the same electrochemical cell where the TBHP is generated.

It was also observed that in absence of TBHP the isborneol in a suitable inert organic solvent also gets oxidised at lead dioxide anode, but the camphor thus obtained did not show any optical activity.

In the absence of TBHP, oxidation of isborneol perhaps proceeds by adsorption of substrate on electrode surface and thereby a carbonium intermediate is generated.



This intermediate reacts with nucleophile like water, present in the electrolyte leading to camphor.

DISCUSSION

The anodic oxidation at a lead dioxide electrode occurs at a potential quite close to the redox potential of PbO_2/PbO , which suggests the catalytic behaviour of anode. It was found that lead dioxide, as a chemical oxidant, also brings about the oxidation of isborneol to camphor.

During the oxidation studies it was observed that optically active camphor does not form in presence of TBHP if the transition metal ion like Mn^{2+} , Co^{2+} , Cu^{2+} , or Ni^{2+} are absent.

The $3d^{n-1}$ metal ion-TBHP gave high stereo selectiveness in the oxidation which may be due to the Syn transfer of hydrogen within the ternary-metal substrate hydroperoxide complex. In other words, the intramolecular transfer of hydrogen to one face of the substrate within a ternary metal substrate hydroperoxide complex may result in the stereospecific oxidation.

The stereoselective oxidations with alkyl hydroperoxide are carried out in the presence of a chiral ligand like (+) or (-) diethyl tartrate [8]. In all such methods the stoichiometric quantities of chiral ligand and alkyl hydroperoxide are required. In the present work, there is no such limitation of carrying out the reaction with the help of chiral active ligand in stoichiometric quantities. The orientation of organic molecule takes place in the bulk.

The polarization curves (Fig.1) are recorded in preparative electrolysis conditions. All the polarization curves are plotted in 1N sulphuric acid medium containing depolarizer, t-butyl alcohol and transi-

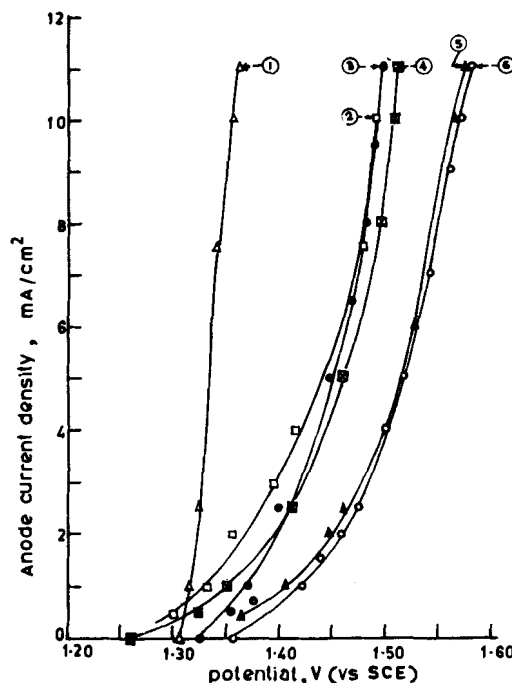


Fig. 1: Polarization curves for the oxidation of isborneol
 1. TBA in 1N H_2SO_4 + isborneol (20 mg per ml)
 2. TBA in 1N H_2SO_4 + isborneol (20 mg per ml) + $3d^{n-1}$ ion (4.503×10^{-4} g.per.ml)
 3. $3d^{n-1}$ metal ion (4.503×10^{-4} g.per.ml) in 1N H_2SO_4
 4. TBA in 1N H_2SO_4 + $3d^{n-1}$ metal ion (4.503×10^{-4} g.per.ml)
 5. TBA + 1N H_2SO_4 of equimolar solution
 6. 1N H_2SO_4 solution

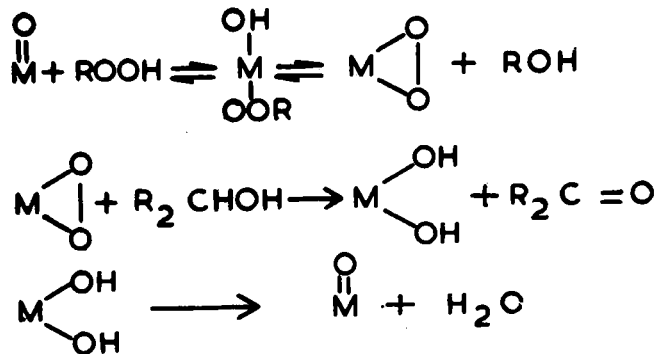
tion-metal cation of $3d^{n-1}$ series like Mn^{2+} . In the absence of transition metal ion, the potential shifts to lower value, which indicates that isborneol gets adsorbed at the electrode surface and results in the oxidation of isborneol; but in the presence of metal ion, the curve gives well defined loop without hysteresis and with the formation of (+) camphor.

The polarization curve in the presence of t-butyl alcohol has the same characteristics as of lead dioxide anode in 1N H_2SO_4 , suggesting that wetting of anode surface by organic phase does not take place. In the presence of both metal ion and t-butyl alcohol, the potential shifts to lower value and is well-defined, indicating the formation of alkyl hydroperoxide complex with metal ion during the electrolysis. This curve remains almost the same in the presence of isborneol indicating the isborneol reacts with alkyl hydroperoxide-metal complex and the reactive species is TBHP-metal complex. It is believed that oxidation takes place in the organic phase containing metal-ion-alkyl hydroperoxide complex quite close to the anode surface, unlike in the absence of metal ion, where the reaction occurs due to adsorption of organic moiety on surface, in a way comparable with chemical oxidation.

Isolation

The isolation of the oxidation product was carried out by first neutralizing the organic phase with sodium bicarbonate. The neutralized phase was subjected to vacuum distillation. The distilled phase gave two products, namely, t-butanol and t-butane.

The camphor thus obtained (residue) was recrystallized from absolute ethyl alcohol and melting point was checked, 181°C (uncorrected). The optical activity (+) of the camphor in alcohol (20% w/v) thus obtained was measured at 589 nm and found to be +44, which shows



where R_2CHOH = organic substrate, RO_2H = t-butyl hydroperoxide, M = metal ion of 3d transition series.

that (+) camphor is formed during the oxidation of isoborneol. From the aqueous phase neutralized with sodium bicarbonate, the 10 camphor sulphonic acid was isolated, and this had an optical rotation of $+24^\circ$. The IR spectrum of each sample was recorded and showed absence of isoborneol in an isolated sample.

Equation for the oxidation can be written as

CONCLUSION

The method reported herein for stereospecific synthesis will find its major application in the synthesis of chiral epoxides, which constitutes

ideal building blocks for the asymmetric synthesis of complex molecules. TBHP is a mild oxidant in organic synthesis. In combination with a variety of transition-metal catalysts, it can bring about the diverse selective oxidative transformations. The mechanism at present is not properly understood. The alkyl hydroperoxide has a potent application in the development of processes for the conversion of olefin, feedstocks obtained in petrochemical industries during refining process, into useful oxygen containing derivatives by proper choice of metal catalyst coupled with alkyl hydroperoxides.

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