

## ELECTRO-OXIDATION UNDER PHASE TRANSFER CONDITION

DINESH CHANDRA TRIVEDI

Central Electrochemical Research Institute, Karaikudi - 623 006

### ABSTRACT

A new redox phase transfer catalyst is reported, which in its oxidised form is soluble in non-polar organic phase and in the reduced form is soluble in aqueous phase. The reduced form gets oxidised at anode surface and gets transferred to non-aqueous medium, where this brings about the oxidation of organic substrate, which is otherwise not possible due to factors like non-solubility in aqueous phase, steric hindrance etc. By this technique 1,7,7 trimethyl bicyclo heptane-2-ol (isoborneol) and 2,2 dimethyl 3-methylene bicyclo (2,2,1) heptane (camphene) have been selectively oxidised.

**Key words :** Phase transfer catalysis, Steric hindrance, camphor

### INTRODUCTION

A two-phase technique that shows great promise for the application of a variety of synthetic reactions is "phase transfer catalysis", the process in which reaction is brought about by the transfer of one reactant across interface into the other phase where the desired reaction can proceed. The phase transfer agent is not consumed because the transport function is performed repeatedly. Invariably the transferred species is an anionic nucleophile ( $Nu^-$ ) [1-10]. This method is advantageous in synthetic organic electrochemistry; the oxidant is continuously regenerated electrochemically at an anode like lead, the cathodic reaction being hydrogen evolution. The product yield is much higher. In this communication, the oxidation of 2,2 dimethyl 3-methylene bicyclo (2,2,1) heptane (camphene) and (isoborneol) 1,7,7 trimethyl bicyclo heptane-2-ol to 1,7,7, trimethyl bicyclo heptane-2-one (camphor) under phase transfer conditions in presence of cetyl trimethyl ammonium chromate (CTAC) as a phase transfer agent (PTA) is reported.

### EXPERIMENTAL

The electrolysis was carried out at lead dioxide anode. An emulsion formed with 1 N  $H_2SO_4$  in water and benzene or ether in equal volumes containing camphene and PTA was used as electrolyte.

Electrolysis was conducted at 310°K in an undivided cell equipped with 10 cm<sup>2</sup> apparent area of lead dioxide anode, prepared by anodising high purity lead for one hour in 2 N  $H_2SO_4$  at a current density of not more than 20 mA.cm<sup>-2</sup>. A lead sheet wrapped with blue asbestos was used as cathode. Before use, this asbestos was washed thoroughly with sulphuric acid and rinsed with water and acetone and dried at 383°K to remove any organic impurity from the material.  $Hg/Hg_2SO_4$  was used as a reference electrode. The potential of the anode was controlled with a potentiostat coupled with integrator to monitor the charge.

#### Synthesis of Phase Transfer Agent (PTA)

The PTA used in this work is cetyl trimethyl ammonium chromate. This is prepared from cetyl trimethyl ammonium bromide [ $CH_3(CH_2)_{15}(CH_3)_3NBr$ ], by adding potassium chromate in stoichiometric quantities. On addition of potassium chromate solution, a thick yellow precipitate of the highly insoluble chromate compound separates out. This is correctly identified by its characteristic IR spectra.

This bis (cetyl-trimethyl-ammonium) chromate was found to be highly soluble in all non-polar solvents like benzene, toluene, chloroform,

methylene chloride etc. Its reduced form which gives  $Cr^{3+}$  ion is soluble in aqueous medium. The emulsion was formed with 50 ml of benzene and 50 ml of aqueous phase containing 1 N  $H_2SO_4$ , PTA (100 mg) and 1 M solution of camphene in benzene or ether. Emulsification was achieved with a magnetic stirrer which is found necessary to prevent the separation of the two phases.

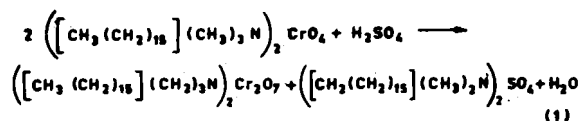
After electrolysis, the organic phase was separated and evaporated under vacuum. The residue was taken up with water and extracted with ether. The washing of the residue with water is essential to remove any inorganic impurities of trivalent chromium formed during the redox process. The isolated products were characterised by their oxime and hydrazone derivatives and I.R. Spectrum. The polarisation curves (I-E) were recorded in preparative electrolysis conditions.

### RESULTS AND DISCUSSION

In all experiments, isoborneol gave the ( $\pm$ ) camphor exclusively without any side product, but camphene, on electrolysis by passing the theoretical amount of current, gave a mixture of isoborneol, borneol and camphor. The results obtained with bis-C.T.A.C indicate that neither the anodic potential nor the current density significantly affect the nature and yield of the final product, but these electrochemical parameters do affect the regeneration of  $Cr_2O_7^{2-}$  ion from  $Cr^{3+}$  present in the aqueous phase.

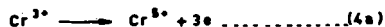
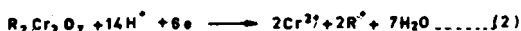
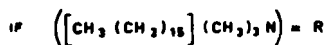
The normal electrooxidation of  $Cr^{3+}$  salt in sulphuric acid medium at lead dioxide anode is affected by the presence of  $Cr_2O_7^{2-}$  formed during the electrolysis. But the situation here is different. Here, as soon as  $Cr_2O_7^{2-}$  is regenerated at the anode surface, it is transferred to non-aqueous immiscible layer by phase transfer agent viz. CTA, and hence there is no  $Cr_2O_7^{2-}$  present in the aqueous solution to affect the electro-oxidation of  $Cr^{3+}$  to  $Cr^{6+}$ . Hence, this method of regeneration of  $Cr^{6+}$  is highly economic in many ways, the first and foremost being the energy saving. In the method described here, one can achieve current efficiency of 90-100% if the parameters are properly chosen like i) current density ii) inter electrode distance and iii) agitation.

Looking to the reaction conditions and product analysis, the following mechanism is suggested for the PTA.



HIGHLY SOLUBLE IN ORGANIC NON POLAR SOLVENTS

SOLUBLE IN AQUEOUS PHASE



SOLUBLE IN AQUEOUS PHASE

REGENERATED SOLUBLE IN ORGANIC PHASE

It is an established fact that  $\text{CrO}_4^{2-}$  ion gets dimerized in presence of proton, as indicated in the equation (1). This dichromate salt of CTA cation is highly soluble in non-polar organic solvent; the reason for this high solubility is perhaps due the hydrophobic nature of very large cationic size of cetyl trimethyl ammonium ion and increased covalent character of PTA.

As is evident from equations (1), (2) and (3), CTA cation forms salt with  $\text{SO}_4^{2-}$  and this salt helps in micellization of organic phase with water due to lipophilic character of cation.

The  $\text{Cr}_2\text{O}_7^{2-}$  anion on reduction gives the  $\text{Cr}^{3+}$  cation which is highly hydrophilic and hence goes to aqueous phase. This redox cycle comprising of hydrophilic character of anion and cation has been used successfully (equations 4a, 4b).

The oxidation of 1,7,7 trimethyl bicycloheptane 2-ol (A) and 2,2 dimethyl 3-methylene bicyclo (2,2,1) heptane (B) to camphor (C) can be represented by equation (5). (See drawing below)

The standard potential of  $\text{Cr}_2\text{O}_7^{2-} + 6\text{e} \rightarrow 2\text{Cr}^{3+}$  is +1.33 V. The oxidation potential of this redox couple is highly dependent on acid concentration; in the present case, the oxidation potential of the couple is +1.3 V.

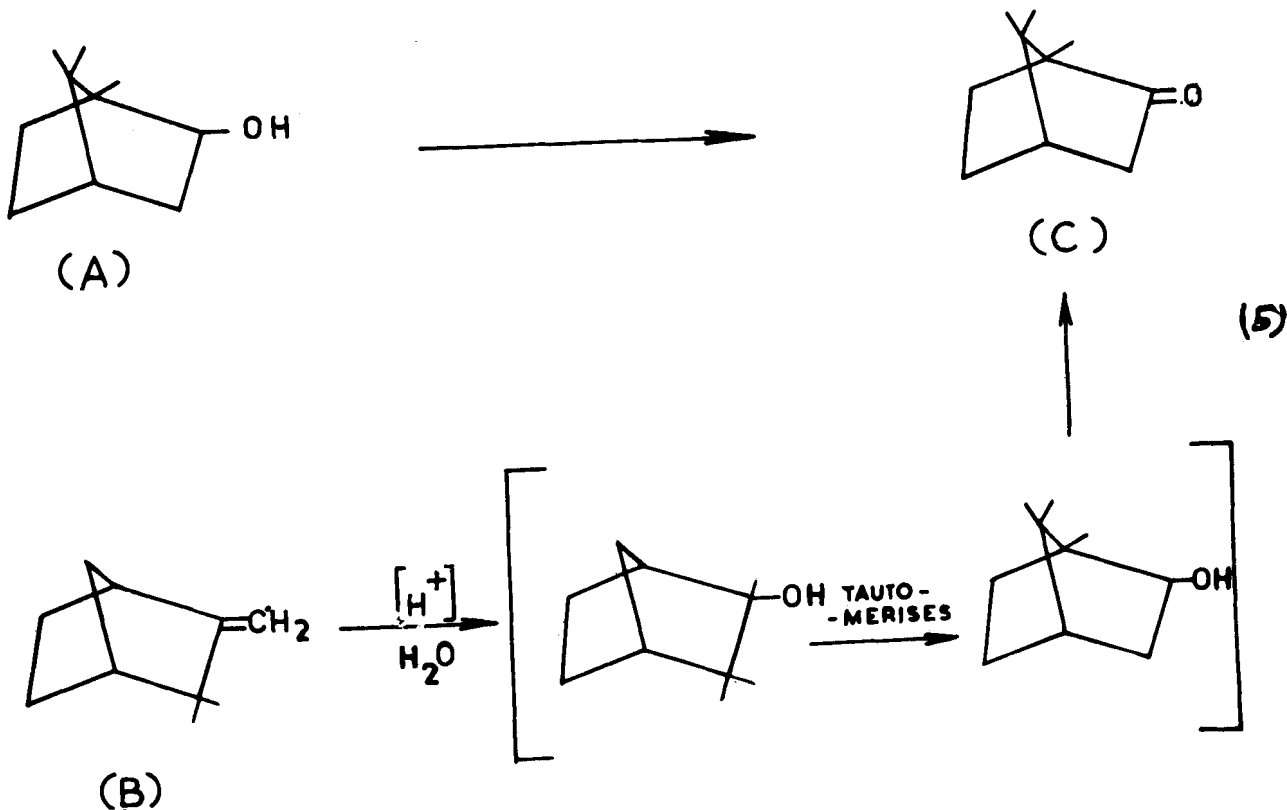
Table I describes the current efficiencies achieved in actual preparative electrolysis conditions at lead dioxide anode in the presence and absence of PTA, namely CTAC.

Table I: Current efficiencies obtained at lead dioxide anode with and without PTA

Anode C.D:  $5 \text{ A.dm}^{-2}$

Medium	Cell voltage (V)		Current efficiencies (%)	
	Without PTA	With PTA	Without PTA	With PTA
1 N $\text{H}_2\text{SO}_4$	5 V	4.9 V	62.5	84
2 N $\text{H}_2\text{SO}_4$	4 V	3.8 V	74.16	90
3 N $\text{H}_2\text{SO}_4$	3 V	2.7 V	76.6	98

In the absence of PTA, the current efficiency of reaction is poor mainly due to the presence of  $\text{Cr}_2\text{O}_7^{2-}$  at anode surface which promotes the evolution of oxygen. For the transfer of  $\text{Cr}_2\text{O}_7^{2-}$  from the aqueous phase to the organic phase, the tetrabutyl ammonium and tetraethyl ammonium cations were also tried in addition to cetyl trimethyl ammonium cation. The cetyl trimethyl ammonium cation is more hydrophobic than tetrabutyl ammonium or tetraethyl ammonium cation and hence the transfer of  $\text{Cr}_2\text{O}_7^{2-}$  is better performed by CTA than by the other two and the details of which will be communicated later.



All the polarization curves plotted are similar. The possibility of the working electrode being covered by the organic phase cannot be ruled out (Eq. (1) and (3) where PTA forms the compound with sulphate ion). This phenomenon may cause adsorption of cationic surfactants at the interface.

Table I gives clear indication that the current efficiencies are better in presence of PTA and hence it is believed that oxidation of organic substrate takes place in the organic phase next to the anode surface. This observation is supported by the fact that the yield of product and current efficiency increases with the rate of agitation.

### CONCLUSION

With the use of PTA, the oxidation presumably proceeds at interface of non-aqueous and aqueous phase and with  $\text{Cr}_2\text{O}_7^-$  as an oxidant, the reaction with isoborneol or camphene (camphene hydrate) proceeds via chromate ester intermediate. This reaction which is an example at the phase boundary, can be taken with advantage to use liquid-liquid interface to control or alter the stereochemistry of the organic substrate. The insoluble CTAC, perhaps, can also be used for ion selective electrode for the determination of hexavalent present in the industrial effluent and also for its removal.

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