

ELECTROCATALYTIC GLYCOL CLEAVAGE BY PERIODATE / IODATE REDOX SYSTEM UNDER PHASE TRANSFER CONDITIONS

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Oxidative cleavage of glycols and related compounds by electrogenerated periodate in a 2-phase anolyte employing phase transfer catalysis is reported. A divided cell with lead dioxide anode is used to generate periodate which is transferred to the organic phase where oxidation takes place. The iodate formed in this step is transferred back to the aqueous phase and reoxidises to periodate at the anode, completing the catalytic cycle. Iodate can be taken in substoichiometric quantity. Conversion and selectivity for aldehyde are high in the oxidation of hydrobenzoin, benzoin and erythro -9, 10-dihydroxyoctadecanoic acid.

Keywords: Redox system, phase transfer catalysis, oxidation cleavage.

INTRODUCTION

Periodate is a selective reagent for the oxidative cleavage of vicinal diols and related compounds like hydroxyketones, diketones and aminoalcohols [1]. Sodium periodate is particularly useful for the oxidation of water soluble substrates. When the substrate is insoluble in water, a solvent such as methanol where substrate and oxidant have reasonable solubility has to be used. Alternately, phase transfer catalysis can be employed advantageously [2].

Electrogenerated periodate [3] has been used for glycol cleavage as in the generation of acetaldehyde from 2,3-butanediol [4]. Since 2,3-butanediol is soluble in water, there are no solubility limitations. However further anodic oxidation of acetaldehyde to acetic acid at the same potential as is used for the periodate generation, adversely affects selectivity. To overcome this, an "ex-cell" process was adopted [5]. Use of electrogenerated periodate has not been reported for water insoluble glycols except for a patent on Lemieux - Rudolf type cleavage of carbon - carbon double bond by periodic acid [6]. Both solubility limitations and poor selectivity due to further oxidation of the product aldehyde are anticipated. The present paper deals with the use of phase transfer catalysis which effectively overcomes both these limitations

EXPERIMENTAL

An H-type cell whose anode compartment was 45 mm and cathode compartment, 30 mm in diameter tube with G-4 sintered disc, was used. The lower edge of the connecting tube was about 35 mm from the bottom of the anode

compartment. The anode compartment carried the lead dioxide sheet (0.3 x 10 x 50 mm) anode and the reference electrode (SCE). The cathode was lead sheet (0.3 x 10 x 50 mm). The anode and cathode were positioned with the flat surfaces facing each other across the connecting tube. In the two-phase experiments it was ensured that the anode was positioned above the dichloromethane layer. Stirring of the anolyte was done magnetically. Anolyte, 115 ml aqueous sodium sulphate (0.75 M) and catholyte, 50 ml of the same solution were taken. To the anolyte was added the required amount (see Table I) of sodium periodate. The substrate (4.6 mmol) in 35 ml of dichloromethane and 0.5 g of tetrabutylammonium hydrogen sulphate (if used), are also taken in the anode compartment. Electrolysis was done at constant current of 0.2 A, the anodic potential being 2 - 2.5 V(SCE). In a typical experiment with 1.00 g of hydrobenzoin, after electrolysis for 10 hr, the dichloromethane layer was washed with water, directly analysed by GC and evaporation of solvent, gave benzaldehyde in nearly 100% yield.

RESULTS AND DISCUSSION

Hydrobenzoin, benzoin and erythro -9,10-dihydroxyoctadecanoic acid were used as the substrates. An H-type cell with a sintered glass diaphragm was used for the electrochemical studies, with a lead dioxide sheet anode and lead sheet cathode and magnetic stirring of anolyte was done. Reference electrode (SCE) was positioned near the anode.

The aqueous electrolyte was 0.5 M sodium sulphate with added sodium metaperiodate and tetrabutylammonium hydrogen sulphate in the anolyte. The organic substrate was

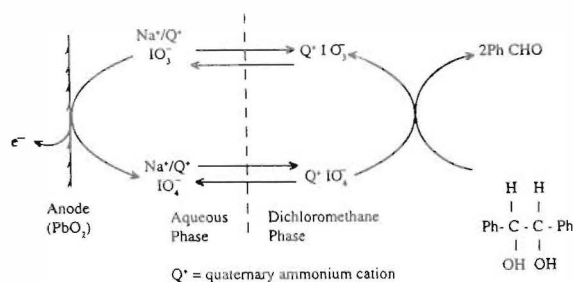
dissolved in dichloromethane which formed the lower layer in the anode compartment in the portion of the H-type cell below the level of the tube connection the two limbs, when not stirring. After the electrolysis, the dichloromethane layer was separated, washed with water and directly analysed by gas chromatography on SE-30 column temperature programmed from 373-493 K. The results with hydrobenzoin are presented in Table I. Similar results were obtained with benzoin and erythro-9, 10-dihydroxyoctadecanoic acid. The former yielded equimolar quantities of benzaldehyde and benzoic acid, and the latter, nonanol and azelaaldehydic acid. The last two were separated by alkali and identified by spectra. The keto alcohol, benzoin was oxidised at a slower rate than the diol. In this, with 5 mmol benzoin and 30 mmol of iodate, the conversion was 58% and with 1.5 mmol iodate, it was 48%. It is known that the rate of oxidation of diol > ketoalcohol > diketone.

Under the conditions of the experiment, direct (unmediated) oxidation did not take place (as seen from Table I). In nonaqueous solvent (methanol) using carbon electrodes, a variety of glycols have been cleaved to the carbonyl compounds or their acetals by anodic oxidation [7]. In the present study even though the anode was maintained > 2 V, potential adequate for the oxidation of glycols, absence of oxidation is clearly due to insolubility in the aqueous phase. The subsequent experiments deal with electrogenerated periodate for mediated oxidation. Sodium iodate was oxidised to periodate at the lead dioxide anode in 0.5 M sodium sulphate solution at 2.0 V with a current efficiency of 85%. However in the absence of a phase transfer catalyst, this was not capable of oxidising the substrate present in the dichloromethane solution (Table I). With added phase transfer catalyst the oxidation proceeded smoothly and with high selectivity to the aldehyde. In initial experiments, excess iodate was taken in the electrolyte (Table I), but subsequent

TABLE I: Electrochemical oxidation of hydrobenzoin

Anolyte composition ²		Phase transfer catalyst ³	Conversion ⁴ (%)
NaIO ₃	Na ₂ SO ₄ M		
Nil	0.75	Nil	0
0.25 g (1 mmol)	0.75	Nil	6
6.48 g (33 mmol)	0.75	0.5 g (1.5 mmol)	100
0.2 g (1 mmol)	0.75	0.5 g (1.5 mmol)	100

- 1 g (4.6 mmol) of hydrobenzoin in each experiment, in 35 ml dichloromethane
- Volume of anolyte 115 ml, excluding dichloromethane
- Tetrabutylammonium hydrogen sulphate
- By G C analysis, product is benzaldehyde



Scheme 1: IO₄⁻/IO₃⁻ mediation in biphasic system

studies showed that sub-stoichiometric quantity of iodate is enough to bring about complete reaction (Table I). The electrogenerated periodate is extracted continuously into the dichloromethane phase, effectively simulating "ex-cell" conditions within the cell itself, thus preventing further oxidation of the aldehyde (See Scheme 1).

CONCLUSION

Electrochemical glycol cleavage by periodate/iodate mediatory system has been shown to be successful for water insoluble substrates when done in a two-phase system of water and dichloromethane along with a phase transfer catalyst. Under these conditions, further oxidation of the product aldehyde is avoided and selectivity is high.

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