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Electrochemical Synthesis of Quinolinic Acid from Quinoline

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Proposed mechanism of conversion of quinoline to quinolinic acid involves 16 e transfer reaction, substantiated by millicoulometry. Effects of electrode material, temperature, concentration of both substrate and anolyte on potentiostatic oxidation revealed high efficiency of Pb/PbO_2 in 70% H_2SO_4 at 60°C.

INTRODUCTION

Galvanostatic oxidation of quinoline to quinolinic acid with Pt gauze anode was first reported by Kulka[1]. Later Cochran and Little[2] extended the work to substituted quinolines on Pt and PbO_2 electrodes. Owing to its practical importance and industrial interest to get nicotinic acid (by thermal decomposition) some brief communications[3-6] mainly intended toward production cost and economy factor have been noticed. Primarily all these studies are concerned with galvanostatic oxidation of quinoline and there is hardly any evidence to controlled potential electrolysis and mechanistic approach.

In this communication, investigations on the potentiostatic oxidation of quinoline in aqueous H_2SO_4 at Pb, Pb/PbO_2, smooth Pt and perforated Pt electrodes have been studied and compared. The possible mechanism for the electrode reaction is highlighted.

EXPERIMENTAL

Chemicals and Reagents

Quinoline was a Farek (Berlin) G.R. while all other reagents were analytical grade.

Electrodes

Electrodes, smooth Pt ($2 \times 2 \times 0.05$ cm), perforated Pt ($2 \times 1.5 \times 0.05$ cm) and PbO_2 deposited on Pb ($2 \times 2 \times 0.2$ cm) were fabricated. Different sizes of grade-I Pb electrodes were prepared.

Controlled Potential Electrolysis

Potentiostatic electrolysis of quinoline was carried out in a three compartment H-shaped glass cell[7] fabricated in the laboratory. 50 ml of a solution of 0.25 M quinoline in 75% H_2SO_4 was used as anolyte in the working electrode compartment and 20% H_2SO_4 as catholyte in the counter electrode compartment. The third compartment served as the

S.C.E. reference electrode. A smooth Pt electrode invariably served as the cathode. A potential of +1.5 V vs. S.C.E. was maintained on the anode by the potentiostat when a current *ca* 500 mA passed through the solution. The temperature was maintained at 60° ± 2° and the anolyte stirred at a constant rate by a magnetic follower. Electromagnetic interference was minimised by all possible means including perspex cover to record genuine potentiostatic readings. Anolyte turned dark brown initially and changed to amber colour toward the end of the reaction after about 12 hr. Theoretical time based upon current and quantity of quinoline is 10.7 hr.

Work Up

Reaction mixture was brought to pH 3 by 30% NaOH solution and resinous material filtered off along with Na_2SO_4. Filtrate at 90°, mixed with hot $CuSO_4$ solution and entire mixture steam-heated for half an hour. The copper chelate of quinolinic acid was filtered off, washed and dried, later suspended in hot water and H_2S gas bubbled in (2 hr) to decompose it completely into quinolinic acid and CuS. Filtrate after removal of CuS was boiled with activated charcoal, filtered, concentrated and cooled when prisms of quinolinic acid crystallized out; recrystallized from water and air dried.

Controlled Potential Coulometry

An indigenous coulometer[8(a)-(b)] was used to determine the value of '*n*' for the electrochemical reaction. 5 ml of 0.01 M quinoline was electrolysed at a Pt tip electrode (*ca* 0.25 cm^2) at +1.5 V vs. S.C.E. for 30 min. A value of $n = 16.3 \simeq 16$, standardized against hydroxyazobezene ($n = 2$) was obtained.

Identification

The colourless and odourless prisms of the electrosynthesised product melted at 188° (reported[9] 190°) when rapidly heated, with decomposition into nicotinic acid. Nitrogen percentage was found to be 8.21% (Calc. for $C_7H_5NO_4$: 8.38%). The polarogram record with Universal Pen Recording Polarograph (Model OH–105, Hungary) in 0.1M HCl (supporting electrolyte) without any maximum suppressor, capillary characteristic 1.99 $mg^{2/3}$ $s^{1/2}$ at $h = 50$ cm, for the deaerated sample of 0.1 mM–1.0 mM quinolinic acid revealed $E_{1/2} = -0.87$ V vs. S.C.E. (−0.83 V vs. N.C.E., reported[10] −0.82 V vs. N.C.E.). The values establish the identity of the compound.

RESULTS AND DISCUSSION

Several experiments were conducted with the variation of temperature, electrode material, concentration of quinoline and H_2SO_4; some typical results are summarised in Table 1. The data reveal that changes in concentration of substrate have no significant effect on the yield of quinolinic acid. Maximum yields are realised in H_2SO_4 of concentrations greater than 70% as can be seen from Table 2. There is a marked decrease in yield when H_2SO_4 concentration is less than 50%. The yield of quinolinic acid increases with increase in temperature and is highest above 60°. The electro-oxidation is most efficient with Pb/PbO_2 and perforated Pt electrodes giving material yield of ca 60% of quinolinic acid above 60° in 75% H_2SO_4. The Pb/PbO_2 competes with the costly perforated Pt electrode. This may be attributed to its almost equivalent oxygen overvoltage and increased surface area as a result of deposition of PbO_2.

TABLE 1

DEPENDENCE OF THE YIELD OF QUINOLINIC ACID ON CONCENTRATION OF QUINOLINE IN 75% H_2SO_4, TEMPERATURE AND ELECTRODE TYPE

(Volume = 50 ml)

(Potentiostatic Oxidation of Quinoline at 1.5 V vs. S.C.E.)

Molar concentration of quinoline (M)	Electrode	Temperature ($t° \pm 2$)	Material yield* (%)
0.25	Perforated Pt	30	45
0.50	Perforated Pt	30	46
1.0	Perforated Pt	30	46
0.25	Smooth Pt	30	30
0.25	Pb	30	26
0.25	Pb/PbO_2	30	43
0.25	Pb/PbO_2	45	51
0.25	Pb/PbO_2	60	59
0.25	Pb/PbO_2	75	60

*Material yield based on non-recoverable quinoline after oxidation.

TABLE 2

EFFECT OF ANOLYTE (H_2SO_4) CONCENTRATION ON THE YIELD OF QUINOLINIC ACID

(Perforated Pt electrode)

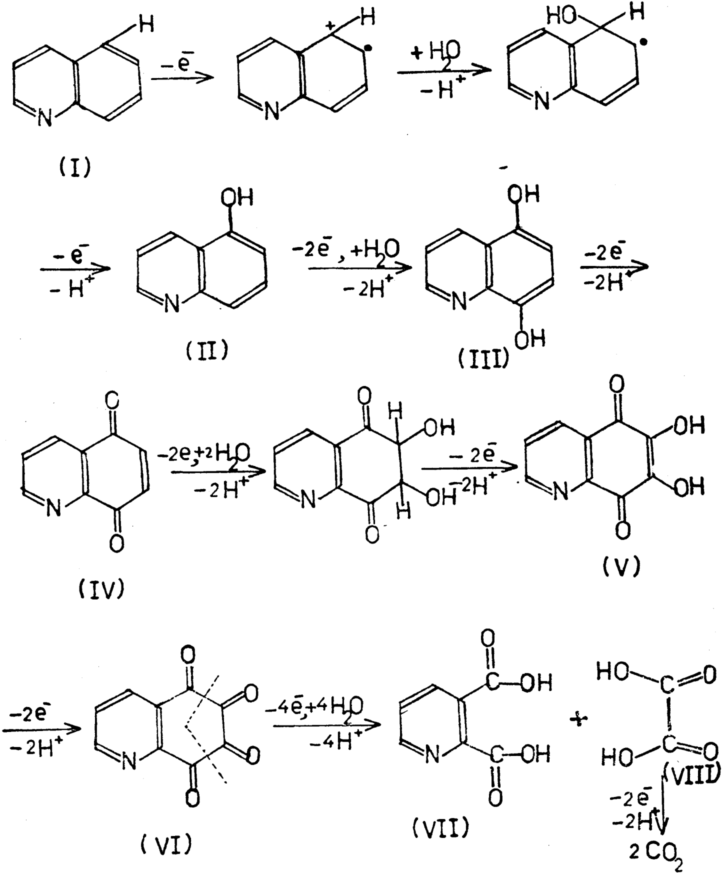
Concentration of H_2SO_4	Yield of quinolinic acid %
30	5
40	10
50	39
60	54
75	60

Mechanism of Electro-Oxidation

White and Lowy[11] studied the anodic oxidation of naphthalene in 1% H_2SO_4 and concluded the sequential formation of α-naphthol, α-naphthaquinone, phthalic acid and α-naphthol-α-naphthaquinone. Based on similar analogy the following mechanism for electro-oxidation of quinoline to quinolinic acid is proposed.

The effect of substituting a nitrogen atom in aromatic framework is to lower the energy of HFMO, thus making it more difficult to oxidise. Contrary to this it is possible to oxidise the adjacent benzene ring more easily as shown in the Scheme 1. In a primary step quinoline (I) undergoes on one-electron oxidation to a cation free radical followed by nucleophilic attack by water to produce 5-hydroxyquinoline (II). The process is repeated in a similar manner to give 5,8-dihydroxy-quinoline (III), which undergoes a rapid two-electron transfer to generate quinone (IV). By a similar series of steps, (IV) transforms into the tetra-one (VI). Consequent upon the fission of quinone ring with simultaneous hydroxylation when 1,2-naphthaquinone is treated with chlorine water yielding dicarboxylic acid, an electrochemical reaction at +1.5 V vs. S.C.E. in which (VI) would

SCHEME 1.



undergo fission to give quinolinic acid by four-electron transfer alongwith hydroxylation is the tenable pathway of reaction. Oxalic acid, a by-product may get oxidised to CO_2. Products (II), (III) and (IV) are relatively stable and their presence in the reaction mixture cannot be ruled out. A total of 16 electrons are involved in the oxidation as confirmed by controlled potential coulometry.

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