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Paired electro-oxidation
Part II: Production of anthraquinone in an undivided cell

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Oxidation of anthracene to anthraquinone by the anodically generated oxidant V^{5+} and both V^{5+} and $\cdot OH$ free radicals generated cathodically was carried out simultaneously in an undivided cell. Both the yield and selectivity of anthraquinone by paired electro-oxidation are higher than that by anodic oxidation only. The maximum total current efficiency for anthraquinone production in the paired electro-oxidation was 151%. A process for anthraquinone production using an undivided cell electrolyser is proposed.

1. Introduction

Anodic oxidation of anthracene for producing anthraquinone has been studied by several investigators [1–4]. Ionic oxidants such as V^{5+}, Co^{3+}, Ce^{4+}, Mn^{3+}, etc. have been generated at the anode surface and used as redox mediators in the oxidation of anthracene to anthraquinone [1–4].

The advantages of paired electrochemical synthesis of organic compounds in a single cell have been reported [5, 6]. Paired electrolysis is much more interesting than that of a single working electrode, especially when both the anodic and cathodic reactions produce the same product simultaneously from the same reactant. In a previous paper [6], paired electro-oxidation of toluene to benzaldehyde in a divided cell was reported.

Anthraquinone may be prepared by anodic oxidation of anthracene in the presence of redox mediators [1–4]. Unfortunately, no paired electro-oxidation of anthracene to anthraquinone has been reported. The V^{5+}/V^{4+} redox couple was chosen in this study. The mechanism of the paired electrochemical oxidation of anthracene to anthraquinone in an undivided cell is as follows.

Anodic reaction:

$$V^{4+} \xrightarrow{k_1} V^{5+} + e^- \qquad (1)$$

Cathodic reactions:

$$O_2 + 2H^+ + 2e^- \xrightarrow{k_2} H_2O_2 \qquad (2)$$

and

$$V^{5+} + e^- \xrightarrow{k_3} V^{4+} \qquad (3)$$

Chemical reactions in bulk solution:

$$C_{14}H_{10} + 6V^{5+} + 2H_2O \xrightarrow{k_4} C_{14}H_8O_2 + 6V^{4+} + 6H^+ \qquad (4)$$

$$V^{4+} + H_2O_2 \xrightarrow{k_5} V^{5+} + \cdot OH + OH^- \qquad (5)$$

$$C_{14}H_{10} + \cdot OH + O_2 \xrightarrow{k_6} C_{14}H_8O_2 + \text{others} \qquad (6)$$

A special cell was designed for the paired electro-oxidation of anthracene in the presence of redox mediators in the undivided cell. The paired electro-oxidation of anthracene was explored and compared with the results of anodic oxidation only.

2. Experimental details

Electrolysis was carried out in a 500 ml undivided cell. Both anode and cathode were platinum plates. The anodic and cathodic overpotentials were measured against two SCE electrodes, respectively, and recorded using a two-pen recorder. The d.c. current was supplied by a galvanostat/potentiostat (Nichia NP-G1005 E). The total amount of electricity passed during a run was measured by a coulometer (Hokuto HF-201). The temperature of the solution was controlled within ±0.5° C. The electrolyte was agitated by double turbines. Oxygen was introduced to the cathodic surface by bubbling through a hollow global glass disperser below the cathode. A reflux condenser was controlled at 0°C by circulating cooling medium for condensing the solvent vapor ($CHCl_3$).

300 ml of H_2SO_4 aqueous solution which contained V^{4+} and 100 ml of anthracene dissolved in $CHCl_3$ organic solution were added to the cell. The agitation rate and temperature were adjusted to the desired values. Then the power supply was switched on.

After electrolysis, the organic products and reactant were sampled and analyzed using a gas chromatograph (Shimadzu GC-8A) with a flame ionization detector and a 3 m column packed with OV–17 on chromosorb W 80/100.

3. Results

3.1. *Anodic oxidation of anthracene*

The results revealed that the detectable products were

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mainly anthraquinone and small amounts of other products. The selectivity of anthraquinone was defined by the mole of anthraquinone produced per mole of anthracene reacted. In general, the yield and selectivity of anthraquinone based on anodic oxidation were comparatively low, as shown in Table 1. The maximum current efficiency and selectivity of anthraquinone were 94.0 and 83.4%, respectively.

3.2. *Paired electro-oxidation of anthracene*

The results of paired electrochemical oxidation of anthracene also revealed that the detectable products were mainly anthraquinone and small amounts of other products. The total current efficiency and selectivity of anthraquinone including both anode and cathode are higher than that for anodic oxidation only as shown in Table 2. The maximum total current efficiency and selectivity of anthraquinone of the paired electro-oxidation were 151.9% and 99.7%, respectively.

4. Discussion

4.1. *Effect of sulphuric acid concentration on the current efficiency and selectivity*

Tables 1 and 2 show that increasing H_2SO_4 concentration increased both the current efficiency and selectivity of anthraquinone. In general, the overpotential to generate oxygen is higher in strong acid solution than that in weak acid solution or alkaline solution [7, 8]. Generation of oxygen on the anode can be inhibited in acidic solution, and this enhances anodic current efficiency as well as the selectivity of anthraquinone.

Increasing the sulphuric acid concentration increases the density of the aqueous solution which becomes similar to the density of chloroform solution resulting in a better suspension of the organic solution in the aqueous solution.

The main cathodic reactions in the absence of bubbling oxygen are

$$2H^+ + 2e^- \xrightarrow{k_7} H_2 \qquad (7)$$

and

$$C_{14}H_{10} + V^{5+}(\text{or } V^{4+}) + e^- \xrightarrow{k_8} \text{pitch-like, sticky byproduct} \qquad (8)$$

On the other hand, the main cathodic reactions are Equations 2 to 6 in the presence of bubbling oxygen. Increasing sulphuric acid concentration increases the H^+ concentration and results in higher H_2O_2 concentration and favours the production of anthraquinone and decreases the sticky byproduct. Both the current efficiency and selectivity for anthraquinone production are significantly promoted by increasing sulphuric acid concentration.

4.2. *Effect of oxygen flow rate on both current efficiency and selectivity of anthraquinone by paired electro-oxidation*

In 10.0 M H_2SO_4 and 5×10^{-3} M V^{4+} aqueous solution and with other operating conditions fixed increasing the oxygen flow rate increased the current efficiency and selectivity of anthraquinone as shown in both Tables 1 and 2. Increasing the oxygen flow rate near the cathode inhibits access of both anthracene molecules and V^{5+} ion to the cathode surface where anthracene may be reduced to byproducts and V^{5+} to V^{4+}. The mechanism of anthracene oxidation by both V^{5+} and $\cdot$OH free radicals in bulk solution involving chain reaction steps are summarized as follows [6, 9–12]

$$C_{14}H_{10} + \cdot OH \xrightarrow{k_9} C_{14}H_9\cdot + H_2O \qquad (9)$$

$$C_{14}H_9\cdot + O_2 \xrightarrow{k_{10}} C_{14}H_9OO\cdot \qquad (10)$$

$$C_{14}H_9OO\cdot \xrightarrow{k_{11}} C_{14}H_8O\cdot + \cdot OH \qquad (11)$$

$$C_{14}H_8O\cdot + O_2 \xrightarrow{k_{12}} C_{14}H_8OO_2\cdot \qquad (12)$$

$$C_{14}H_8OO_2\cdot + C_{14}H_{10} + V^{4+} \xrightarrow{k_{13}} C_{14}H_8O_2 + C_{14}H_9\cdot + OH^- + V^{5+} \qquad (13)$$

The rate of the chain reactions, Equations 10 to 12 can be promoted by increasing the oxygen flow rate. In

Table 1. Production of anthraquinone by anodic oxidation only in an undivided cell

$[H_2SO_4]$ /M	$10^3[V^{4+}]$ /M	*Agitation rate* /r.p.m.	*c.d.* /mA cm^{-2}	*C.e. of AQ** /%	*S. of AQ*[†] /%
4.0	5.0	1000	5.0	29.9	39.7
7.0	5.0	1000	5.0	52.4	60.3
7.0	1.0	1000	5.0	74.3	71.2
7.0	5.0	600	5.0	32.6	59.0
7.0	5.0	1000	3.0	71.2	80.3
10.0	5.0	1000	5.0	94.0	83.4

Temperature: 30° C. Amount of charge passed: 350 C.
Concentration of anthracene: 0.0112 M.
* C.e. of AQ is current efficiency of anthraquinone.
[†] S. of AQ is selectivity of anthraquinone.

Table 2. Production of anthraquinone by paired electro-oxidation in an undivided cell

$[H_2SO_4]$ /M	$10^3[V^{4+}]$ /M	*Agitation rate* /r.p.m.	*c.d.* /mA cm^{-2}	*Oxygen flow rate* /ml min^{-1}	*C.e. of AQ** /%	*S. of AQ*† /%
4.0	5.0	1000	5.0	200	46.3	60.5
7.0	5.0	1000	5.0	200	80.5	82.2
7.0	1.0	1000	5.0	200	85.5	99.7
7.0	5.0	600	5.0	200	40.8	64.4
7.0	5.0	1000	3.0	200	93.3	95.5
10.0	5.0	1000	5.0	100	125.5	91.0
10.0	5.0	1000	5.0	200	151.9	98.0

Temperature: 30° C. Amount of charge passed: 350 C.
Concentration of anthracene: 0.0112 M.
* C.e. of AQ is current efficiency of anthraquinone.
† S. of AQ is selectivity of anthraquinone.

addition, increasing oxygen flow rate near the cathode produces more H_2O_2 which reacts with V^{4+} to generate $\cdot OH$ free radicals and V^{5+}, both of these species can oxidize anthracene to anthraquinone.

4.3. *Effect of V^{4+} concentration on both the current efficiency and selectivity of anthraquinone in paired electro-oxidation*

Generally, during indirect oxidation of organic compounds in an undivided cell by the oxidizing mediator, some of the higher valent oxidizing mediator will be reduced on the cathode to lower valent ones i.e. Reaction 3, resulting in a decrease in current efficiency.

The V^{4+} ion is initially oxidized on the anode to V^{5+} which then reacts with anthracene in the bulk solution. But some of the V^{5+} may be reduced on the cathode to form V^{4+}.

Furthermore, the $\cdot OH$ free radical may be consumed.

$$\cdot OH + V^{4+} \xrightarrow{k_{14}} V^{5+} + OH^- \qquad (14)$$

Reaction 14 has been demonstrated in studies on Fenton's reagent [13–16]. The rate constant of Reaction 14 ($k_{14} = 2.3 \times 10^8$–3.0×10^8 M s^{-1}) [13, 14, 16] is much larger than the rate constant for generation of $\cdot OH$ free radicals, i.e. Reaction 5 ($k_5 = 10$–200 M s^{-1}) [15, 16]. Increasing V^{4+} concentration increases the rate of Reaction 14, and decreases the rate of formation of anthraquinone.

Additionally, the cathodic reaction of anthracene with V^{5+} (or V^{4+}) takes place, i.e. Reaction 8 increases when the concentration of V^{4+} increases. Accordingly, decreasing the V^{4+} concentration decreases the side reactions and byproduct while the current efficiency and selectivity increase as shown in Tables 1 and 2.

4.4. *Effect of current density and agitation rate on the current efficiency and selectivity of anthraquinone*

Increasing the current density decreases both the current efficiency and selectivity of anthraquinone both without and with bubbling oxygen as shown in Tables 1 and 2. Increasing current density increases both anodic byproduct, O_2 [8, 17], and cathodic byproducts of anthracene, resulting in a decrease in both current efficiency and selectivity.

Increasing the agitation rate causes better distribution of the organic phase in the aqueous phase, resulting in better reaction of V^{5+} with anthracene, and the reaction of H_2O_2 with V^{4+} near the cathode to produce more $\cdot OH$ free radicals and V^{5+}. Thus, increasing the agitation rate increases the transfer of reactants at the interface of this two-phase system, and thus increases in both the current efficiency and selectivity for anthraquinone as shown in Tables 1 and 2.

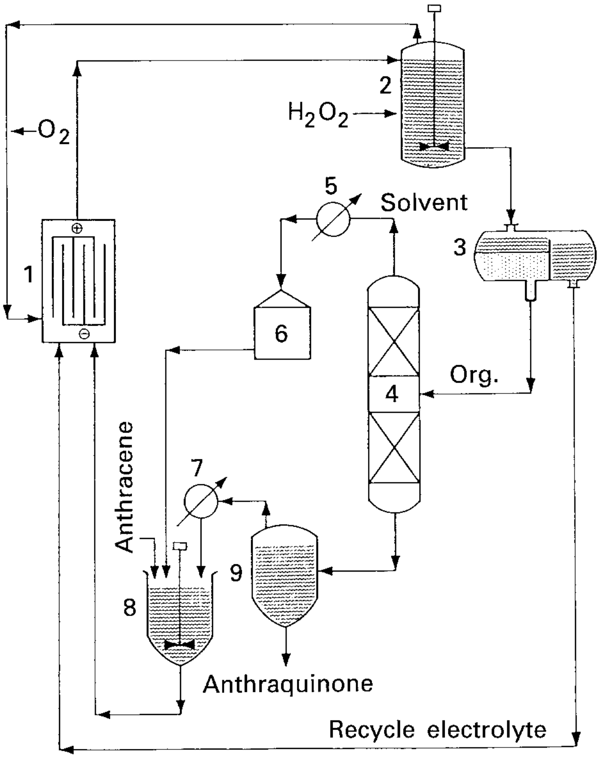

Fig. 1. Flow scheme for the paired electro-oxidation of anthracene anthraquinone. (1) Electrolytic cell, (2) chemical reactor, (3) separator for the separation electrolyte and the organic, (4) distillation tower, (5) condenser, (6) solvent ($CHCl_3$), storage tank, (7) condenser, (8) organic reactant preparation tank, (9) crystallizer.

4.5. *Paired electro-oxidation process*

In a previous paper [12], a schematic flow diagram for paired electro-oxidation of toluene to benzaldehyde in a divided electrolyser was reported. A schematic flow diagram for paired electro-oxidation is now proposed involving an undivided electrolysis cell, a chemical reactor, a separator for separating the electrolyte and organic compounds, a distillation column for the recovery of solvent ($CHCl_3$) and crystallizers for separating anthraquinone and solvent, respectively, as shown in Fig. 1.

However, both the $\cdot OH$ free radical and H_2O_2 are active. The decomposition of H_2O_2 produces H_2O and O_2 and the reaction of $\cdot OH$ free radicals with V^{4+} forms OH^- in the bulk solution. An electrolysis cell with parallel electrodes will decrease the space of bulk solution between the electrodes, as shown in Fig. 1, and in turn decrease the decomposition of H_2O_2 and formation of OH^-, respectively, resulting in high current efficiency for anthraquinone.

According to Reactions 9 to 13, the reaction between anthracene and $\cdot OH$ free radicals as well as V^{5+} is a chain reaction. Although the current efficiency of cathodic reduction of oxygen to produce hydrogen peroxide and anodic oxidation of V^{4+} to form V^{5+} are small, the paired electro-oxidation of anthracene to anthraquinone still has a very high current efficiency since both $\cdot OH$ free radicals and V^{5+} initiate and take part in the chain reactions. Therefore, the paired electro-oxidation process with parallel electrodes is attractive and may become a commercial process for producing anthraquinone.

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