SHORT COMMUNICATION

The electrochemical reduction of anthraquinone to anthrone in concentrated H_2SO_4

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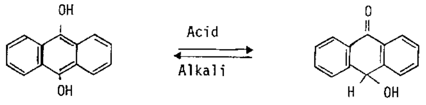
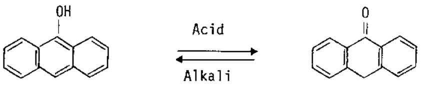
1. Introduction

The chemical reduction of anthraquinone leads to a variety of products. Sodium hydrosulphite ($Na_2S_2O_4$) gives the disodium salt of anthrahydroquinone (I) tautomeric with oxanthranol (II) [1].



(I) (II)

Iron reduces anthraquinone in concentrated sulphuric acid to anthrone (III) [2] tautomeric with anthranol (IV).



(IV) (III)

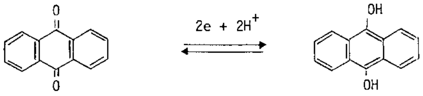
Other reducing agents give dianthraquinonyl [3], anthracene and hydrogenated anthracenes [1].

On the industrial scale these reactions have, however, at least two disadvantages:

(a) large excess of reducing agent is used
(b) large amounts of waste-water are formed.

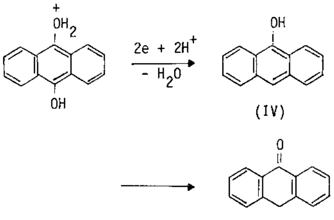
The electrochemical method is an alternative which may overcome these disadvantages:

The electrochemical reduction of anthraquinone has been studied by Lund [4] (in 50 vol% ethanol/50 vol% H_2SO_4 at the Hg cathode) who reports a two-step electrochemical reaction. The first step is a reversible 2*e* reduction of anthraquinone to anthrahydroquinone (I) (tautomeric with oxanthranol).



(I)

and the second step a 2*e* reduction of protonated anthrahydroquinone to anthranol (IV) which is isomerized to anthrone (III).



(IV)

(III)

In preparative electrolysis Lund has found that by controlling the potential at −0.4 V (SCE) further reduction of anthrone is avoided.

In this paper the electrochemical reduction of anthraquinone in concentrated H_2SO_4 (16 mol dm^{-3}) is examined using different cathode materials to identify the optimum conditions for anthrone (III) formation. Anthrone is an intermediate in the preparation of 1,9-benzanthrone an important starting material for the preparation of a group of fast vat dyes.

2. Experimental procedure

Preparative electrolysis was carried out at constant current density in an electrolytic cell of 150 cm^3 capacity. The cathode was made of the metal under study and the anode was a platinum spiral enclosed in a 10 cm^3 porous porcelain pot. Stirring was provided by a magnetic bar.

Anthraquinone and its reduction products were extracted from the reaction medium and analysed by liquid and thin layer chromatography using toluene as eluant. Polarization curves were obtained using a rotating graphite electrode (0.05 cm^2) with standard equipment (Tacussel-France).

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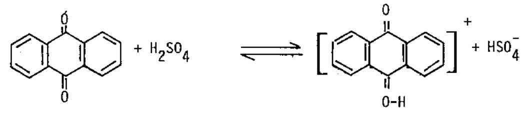
3. Results and discussion

3.1. *Preliminary evaluation of electrolyte and conditions of electrolysis*

3.1.1. Choice of electrolyte. Anthraquinone is soluble in concentrated H_2SO_4 by formation of the oxonium ion [1].



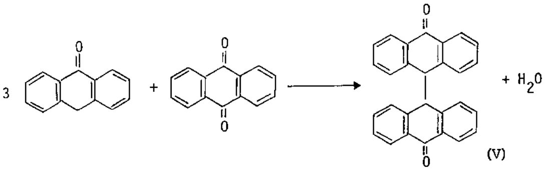
This equilibrium depends on the acid concentration, thus below 14 mol dm^{-3} H_2SO_4 the oxonium ion is formed only to a small extent and the solubility of anthraquinone is very low. At higher H_2SO_4 concentration (above 15 mol dm^{-3}) the solubility of anthraquinone increases (0.1–0.5 mol dm^{-3}).

3.1.2. Choice of temperature. Anthraquinone is stable in 15–17 mol dm^{-3} H_2SO_4 at 100° C in contrast to anthrone which can be oxidized by concentrated H_2SO_4 giving tarry materials and sulphur dioxide.

anthrone + 2 H_2SO_4 → tarry materials + 2 SO_2

Fig. 1 shows the rate of anthrone decomposition in 16 mol dm^{-3} H_2SO_4 as a function of temperature. Increasing the temperature results in a considerable increase in the rate of anthrone decomposition.

Another side reaction is the formation of dianthraquinonly (V) by condensation of anthrone with anthraquinone [5].



The rate of this side-reaction decreases considerably at low temperature (<60° C). Thus the electrochemical reduction an anthraquinone to anthrone must be effected at relatively low temperature (<60° C).

3.2. *Electrochemical measurements*

Fig. 2 shows steady-state polarization curves for the reduction of anthraquinone at a graphite electrode in 16.3 mol dm^{-3} H_2SO_4 at 60° C; for comparison the polarization curve of the solvent is also given. In the presence of anthraquinone two waves prior to H_2SO_4 decomposition appear.

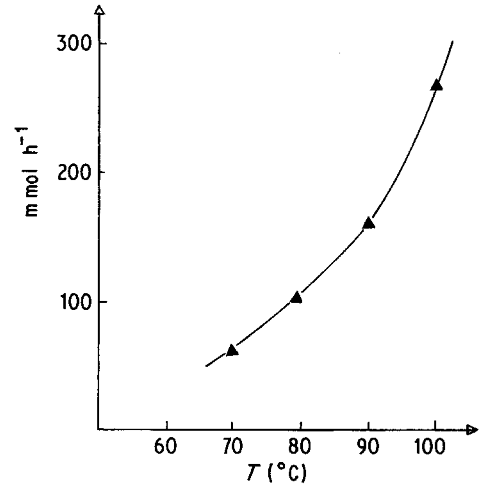


Fig. 1. Rate of anthrone decomposition in 16 mol dm^{-3} H_2SO_4 as a function of temperature. Concentration of Anthrone: 0.48 mol dm^{-3}. Volume of solution is 75 cm^3.

Thus we can postulate a mechanism similar to that proposed by Lund [4] in which anthraquinone is reduced to anthrone in a two-step electrochemical reaction. The first step is a 2*e* reduction

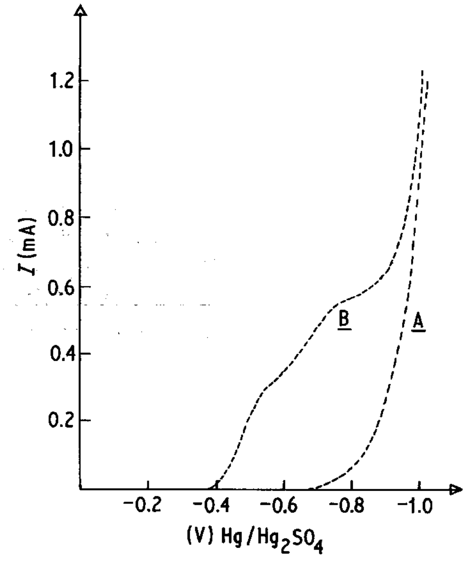


Fig. 2. Steady-state polarization curves at a rotating graphite disk (3.500 rpm). Electrode surface: 0.05 cm^2. (A) 16.3 mol dm^{-3} H_2SO_4. (B) 16.3 mol dm^{-3} H_2SO_4 + 2 × 10^{-2} mol dm^{-3} anthraquinone.

Table 1. Current efficiency of anthrone formation and corrosion rate of different cathode materials. H_2SO_4: 16 mol dm^{-3} concentration of anthraquinone: 0.4 mol dm^{-3} $i = 50$ mA cm^{-2}, $T = 60°$ C

Cathode material	*Charge passed (F mol^{-1})*	*Corrosion (mg Ah^{-1})*	*Current efficiency (%)*
Pt	3.6	<0.1	74
Ag	3.6	3.5	65
Pb	3.6	23.3	48
Graphite	3.2	–*	42
Cu	5.4	184.4	36
Ni	3.6	104.8	11

* There is an increase in weight due to the formation of a polymer layer

of anthraquinone to anthrahydroquinone (I) (which is isomerized to oxanthranol (II)) and the second step a 2*e* reduction of oxanthranol (II) to anthranol (IV) (which is isomerized to anthrone(III)).

3.3. *Preparative electrolysis*

The influence of current density and cathode material on the current efficiency of anthrone formation has been studied.

3.3.1. Influence of current density. Concentrated H_2SO_4 (above 15 mol dm^{-3}) can be reduced at the cathode giving H_2, H_2S, SO_2 and S [6].

$$H_2SO_4 \rightarrow H_2, H_2S, SO_2, S$$

This side reaction can be considerably decreased if the reduction of anthraquinone is effected at low current density (<50 mA cm^{-2}) and the conversion of anthraquinone is not complete ($<90\%$).

3.2.2. Influence of cathode material. The electrochemical reduction of anthraquinone is effected in 16 mol dm^{-3} H_2SO_4 using different electrode materials. The electrolysis was effected at relatively low temperature (60° C) to decrease the rate of anthrone decomposition and at low current density (50 mA cm^{-2}) to decrease the rate of H_2SO_4 reduction.

Table 1 shows that the current efficiency for anthrone formation is strongly dependent on cathode material. Platinum which has the lower overpotential for H_2SO_4 decomposition [6] gives the better results. This unexpected result may be due to a change of the mechanism of anthraquinone reduction at a platinum cathode, thus the reduction of anthraquinone at platinum is probably effected by adsorbed hydrogen atoms and at the other metals (Pb, Cu, Ni) by the formation of organometallic intermediates. The formation of such intermediates explains the high corrosion rate of these metals [7].

4. Conclusion

The electrochemical reduction of anthraquinone must be effected under the following conditions:

(a) using a two compartment cell
(b) using concentrated H_2SO_4 as the electrolyte (15–17 mol dm^{-3})
(c) working at relatively low temperatures (40–60° C)
(d) using Pt or Ag as the cathode
(e) working at low current density (<50 mA cm^{-2})

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