ANODIC OXIDATION OF ANTHRACENE TO ANTHRAQUINONE**

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ABSTRACT

Anodic oxidation of anthracene to anthraquinone was studied using cerous sulphate, manganous sulphate and vanadous sulphate in the electrolyte. Good efficiency of oxidation could be obtained with cerous sulphate even in a low concentration of sulphuric acid as electrolyte. Manganous sulphate gave high yields only when 60% sulphuric acid was employed as electrolyte. Various parameters which influence the oxidation of anthracene with these agents have been studied. Results obtained with stationary and rotating lead anodes and presented.

INTRODUCTION

Anthraquinone is generally manufactured by dyestuff industries and it is widely used for the production of anthraquinone vat dyes.[1] In the past it was manufactured by oxidising a suspension of purified anthracene in boiling water with sodium dichromate and sulphuric acid.[2] Although the most widely employed process is the ring-closure[3] of o-benzyl benzoic acid, anthraquinone is yet produced in some countries on a large scale from anthracene by the oxidation process either electrolytic[4] or chemical.[5]

It was reported by earlier workers that the electrochemical oxidation[6] of anthracene to anthraquinone could be carried out using electrolytically regenerated chromic acid[7,8] in a two-stage process and also by a single stage process using "oxygen carrier" such as cerous sulphate[9-11], manganous sulphate[12] and vanadous sulphate.[13] However, the earlier patents did not mention the relevant details about current efficiency, yield and purity of the product. Rasch and Lowy[11] developed a grid type of anode which had anthracene in contact with the electrode material and they have reported a maximum current efficiency of 37% for 61% yield of anthraquinone. Recently, Sugino and Shirali[14] studied in detail a single stage process using vanadous and cerous sulphate as "oxygen carrier" and reported an yield of 90% with a current efficiency of 50-52% at a current density of of 0.5 to 1.0 amp/dm^2 in 40-50% sulphuric acid.

Anthraquinone is a substance of great technical importance to our dyestuff industries[1] and is not produced till now by the electrolytic method in this country. Therefore, it was thought worthwhile to investigate this process extensively to determine the optimum parameters for the preparation of anthraquinone.

Rotating anode technique[15] was employed and experiments were conducted to collect classifiable data with the object of getting an almost complete conversion of anthrancene to anthraquinone.

EXPERIMENTAL

Materials: Pure anthracene (m.p. 217°C) and L.R. sulphuric acid were used. All the other chemicals were of technical grade.

Cell: A cylindrical tall-form pyrex 1 litre beaker of dimensions 11 cm diameter × 21.5 cm height with a suitable wooden lid carrying four holes for the electrodes and thermometer was used as the cell (Fig. 1). Two narrow strips of lead cathodes, each 0.2 cm × 16.0 cm were used on either side of a cylindrical lead anode with an effective area of 1.1. sq. cm. The electrolyte was agitated by an electrical stirrer, when the anode was stationary. The temperature of the cell was maintained at the desired level by means of an electrical water bath. The anode potential was measured by Crompton potentiometer and a spot galvanometer using mercury-mercurous sulphate reference electrode in the same concentration of sulphuric acid as in the cell. The different experimental conditions for the anodic oxidation are given in the tables.

Procedure: After taking the electrolyte and the depolariser in the cell, excess current was

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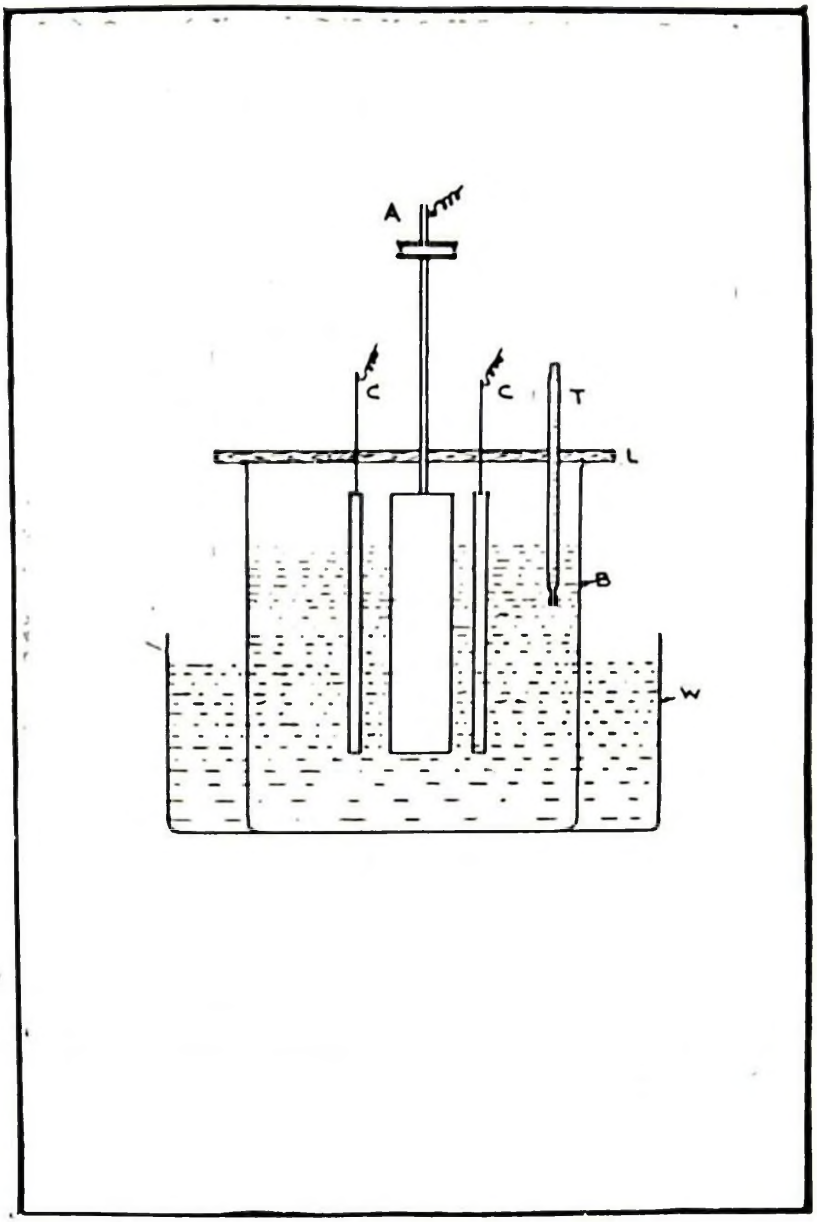


FIG. 1. Electrolytic Cell

A. Anode; *C*. Cathode; *T*. Thermometer; *L*. Lid; *B*. Beaker; *W*. Water bath

passed till a cherry red colour was obtained when manganous sulphate was taken in the electrolyte. When cerous sulphate was taken in the electrolyte, current was passed till a permanent bright yellow colour of the electrolyte was obtained, thereby indicating the complete conversion of anthracene to anthraquinone.

Isolation of the product: After passing more than the theoretical quantity of current, the product was filtered, washed and dried. The m.p. of the product in each run was noted. In a few experiments, anthracene was separated from anthraquinone by treating with alkaline sodium hydrosulphite solution and filtering, the anthraquinone being subsequently regenerated.

Analysis: The purity of the anthraquinone obtained was estimated[16] by reduction with alkaline sodium hydrosulphite, filtering, reoxidising and weighing the precipitated sample.

Large laboratory trials: A 4.2 litre glass beaker was used as a cell for large laboratory trials. A perforated lead sheet with an effective area of 3.7 sq. dm. was used as anode and 2 numbers of lead covered copper rods 5 mm

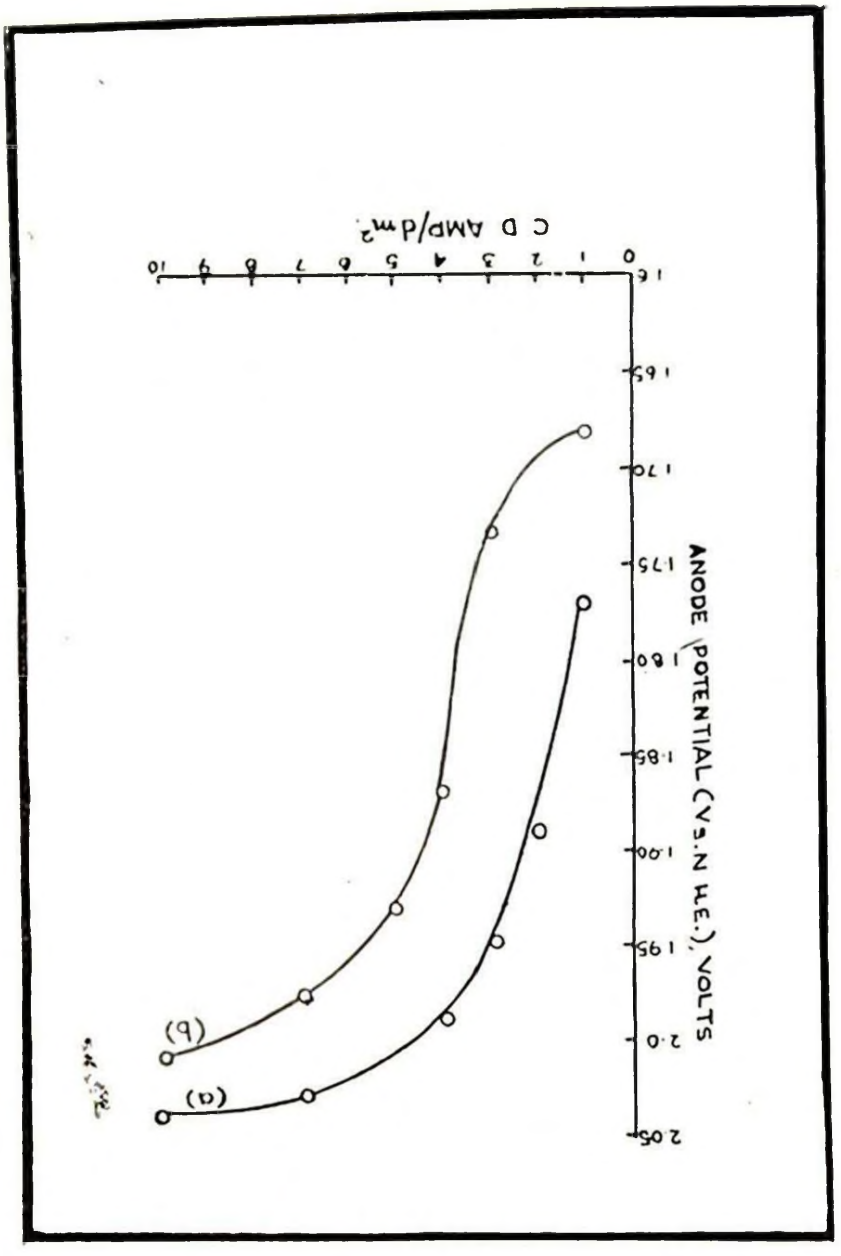


FIG. 2. Plot of anode potential vs current density for (*a*) stationary anode, (*b*) rotating anode.

diameter × 30 cm long (length immersed, 15 cm) were used as cathodes. A glass stirrer giving effective agitation was included in the cell and the cell was kept on an electric heater.

Two litres of 60% sulphuric acid containing 40 g manganous sulphate (anhydrous basis) was the electrolyte. Direct current was passed from a selenium rectifier capable of giving 50 amp at 0-12V. Temperature was maintained at 90-95°C by means of the heater. 200 g of powdered anthracene was suspended in the electrolyte. Same procedure was followed to ensure complete oxidation as was done for small scale experiments.

RESULTS AND DISCUSSION

The influence of rotation of the anode at various current densities is shown in Table I. It can be seen that the current efficiency is higher using rotating anode, especially at higher current densities than with a stationary anode under identical conditions. The current efficiency is low at current densities more than 4 amp/dm² using rotating as well as stationary anodes, and this could be explained well, on the basis of anode potential measurements. The anode potentials determined under rotating and stationary conditions are shown in Fig. 2 and it can be seen that the potential of a

TABLE I

Comparison of the current efficiency and yield with rotating and stationary anodes at different current densities

Electrolyte, 500 cc of 30% sulphuric acid contatning 10 g. ceric sulphate ; Temperature 85-90° C; Anthracene, 5 g (finely powdered and suspended in the electrolyte); R. P. M. of the anode when rotating, 1000.

Expt. No.	*Cell voltage (volts)*	*Current density (amp/dm²)*	*Electricity passed (amp-hr)*	*Motion of anode*	*Anthra-quinone formed (g)*	*Current effici-ency (%)*	*Yield (%)*	*M. P. of Product (°C)*	*Anode potential vs. N. H. E. (volts)*
1	2.0	1	8.25	Rotation	5.6	53.0	95	276	1.68
2	2.0	1	11.2	Stationary	5.0	35.0	86	276	1.77
3	2.5	2	10.5	Rotation	5.2	38.4	90	275	1.69
4	2.5	2	16.8	Stationary	5.4	25.0	91.5	275	1.89
5	3.0	4	10.5	Rotation	5.2	38.4	90	275	1.87
6	3.5	4	16.8	Stationary	2.0	9.9	36.2	281	1.99
7	3.5	10	12.6	Rotation	4.7	28.8	81.0	276	2.01
8	4.0	10	22.0	Stationary	2.7	9.06	46.4	275	2 04

TABLE II

Effect of concentration of sulphuric acid on the current efficiency and yield

Current density, 10 amp/dm² ; Anode, Rotating; Electricity passed, 12.6 amp-hrs. All other conditions are as given in Table I.

Expt. No.	*Concentration of sulphuric acid (%)*	*Anthra-quinone formed (g)*	*Current effici-ency (%)*	*Yield (%)*	*M. P. of product (°C)*
11	20	5.2	34	85	276
12	30	5.4	37.5	91.5	278
13	40	..	..	..	200
14	50	..	..	..	200

The influence of the concentration of cerous sulphate in the electrolyte is indicated in Table III. The current efficiency slightly improves by increasing the percentage of cerous sulphate in the electrolyte.

TABLE III

Effect of concentration of cerous sulphate on current efficiency and yield

Electrolyte, 500 cc of 30% sulphuric acid; Current density, 11 amp/dm^2; Electricity passed, 25 amp-hr. All other conditions are some as in Table I.

Expt. No.	*Concentration of cerous sulphate* (%)	*Anthraquinone formed* (g)	*Current efficiency* (%)	*Yield* (%)	*M.P. of product* (°C)
15	2	4.7	26.5	82.0	277
16	3	4.8	28.8	82.7	276
17	4	5.0	30.0	86.2	276

rotating anode is considerably lower than that of a stationary anode. Whenever the anode potential is well below 1.8 volts on hydrogen scale, good current efficiency was obtained.

The effect of concentration of sulphuric acid in the electrolyte is given in Table II and it can be seen from it that a current efficiency of 37.5% and an yield of 91.5% could be obtained using an electrolyte containing 2% cerous sulphate in 30% aqueous sulphuric acid and a rotating anode. Oxidation is considerably hampered at higher strength of sulphuric acid due to low solubility of cerous sulphate in the same.

The effect of using manganous sulphate in the electrolyte, instead of cerous sulphate, is shown in Table IV. Use of rotating or stationary anode makes very little difference in this case. It is quite interesting to note, however, that even though the anode potential is more than 2.0 volts, a current efficiency of 33.4% and an yield of 94% is obtained at a current density of 2 amp/dm^2 employing stationary anode. It has been noticed, as shown in Table I, that when cerous sulphate is used in the electrolyte, a current efficiency of 9.06 % is obtained at a current density of 10 amp/dm^2 using stationary anode. Under similar conditions using manganous sulphate in the electrolyte the current efficiency is 30%. Even though the anode potential is more than 2.0 volts, in both the cases, it is rather fascinating to note that the difference in current efficiency observed using cerous sulphate and manganous sulphate in the electrolyte is more than 20%. This cannot be attributed to the oxidation potential of the Mn^{3+} - Mn^{2+} system because it is lower than that of the Ce^{4+} - Ce^{3+} system. Higher strength acid used with the former system, perhaps activates the aromatic hydrocarbon and thereby facilitates oxidation. The relative merits of using cerous sulphate, manganous sulphate and vanadous sulphate in the electrolyte are shown in Table V and it can be seen that manganous sulphate can be advantageously employed. It is also noticed that when cerous salt is used in the electrolyte, corrosion of the lead anode occurs and the product obtained is contaminated with lead dioxide particles. With manganous sulphate, corrosion of the anode is negligible and the product obtained is free from lead dioxide and has a better appearance.

The influence of the concentration of anthracene in the electrolyte on the current efficiency and yield of the product is given in Table VI. It can be seen that a concentration of 100/1 of anthracene can be used without much loss in current efficiency. When the concentration of depolariser is below 20 g/l, the current efficiency is low.

Large laboratory scale trials were carried out using manganous sulphate in 60 % sulphuric acid as electrolyte employing stationary anode and the results of the runs are given in Table VII. It may be seen that the results confirm those of the laboratory scale investigation and an yield of 96 % with a current efficency of 48 to 49 % could be obtained.

TABLE IV

Influence of manganous sulphate as "oxygen carrier" on the current efficiency and yield

Electrolyte, 1 litre of 60 % sulphuric acid containing 20 g manganous sulphate; Temperatue, 85-90°C; R.P.M. of the anode 1500; Anthracene, 8 g. finely powdered was suspended in the electrolyte; All other conditions are same as given in Table I.

Expt. No.	*Cell voltage* (*volts*)	*Current density* (*amp/dm²*)	*Motion of anode*	*Anthraquinone formed* (*g*)	*Current efficiency* (%)	*Yield* (%)	*M. P. of product* (°C)	*Anode potential, vs. N. H. E.* (*volts*)
18	2.5	2	Stationary	8.8	33.4	94	282	2.014
	2.5	2	Rotation	8.2	35.6	88	282	1.974
19	2.5	4	Stationary	8.4	31.8	90	282	2.06
20	3.0	6	Stationary	8.2	31.0	88	281	2.09
	3.5	6	Rotation	8.4	27.2	90	281	2.014
21	4.0	8	Stationary	8.4	31.0	90	281	2.13
22	4.5	10	Stationary	8.2	30.0	88	278	2.16
	4.5	10	Rotation	8.9	27.3	95	277	2.084

TABLE V

Results showing comparison of different "oxygen carriers" on the current efficiency and yield of anthraquinone

Current density, 10 amp/dm²; R.P.M. of anode, 1000; Anthracene, 5 g suspended in the electrolyte; Electricity passed, 12.6 amp-hr; All other conditions are same as given in Table I.

Expt. No.	*Cell voltage* (*volts*)	*Electrolyte* H_2SO_4 (%)	*Oxygen carrier*	*Anthraquinone formed* (*g*)	*Current efficiency* (%)	*Yield* (%)	*M.P. of product* (°C)
23	3.5	30	2% Cerous sulphate	4.7	28.8	81	276
24	4.0	60	2% Manganous sulphate	5.0	30	86	277
25	3.5	30	2% Vanadous sulphate	..	..	..	200

TABLE VI

Influence of the percentage of anthracene in the electrolyte on the current efficiency and yield

Electrolyte, 1 litre 60% sulphuric acid, $MnSO_4$ 20 g. Temperature, 90-95°C; Nature of the anode, Stationary; Current density, 4 amp/dm²; All other conditions are as given in Table I.

Expt. No.	*Cell voltage (Volts)*	*Amount of anthracene (g)*	*Duration (hrs)*	*Electricity passed (amp-hr)*	*Anthraquinone formed (g)*	*Current efficiency (%)*	*Yield (%)*	*MP of product (°C)*
26	3.0	8	4.8	20.4	8.4	27.2	90	281
27	3.0	20	11.2	56.0	21.0	29.0	90	282
28	3.0	40	16.5	82.5	39.0	36.5	83.4	281
29	3.0	80	35.0	175.0	82.0	36.5	88.5	281
30	3.0	•100	47.0	235.0	102.0	33.4	87.3	282

• The maximum amount beyond which the stirring of the slurry was ineffective.

TABLE VII

Results of large laboratory scale runs

Electrolyte, 2 litres of 60% sulphuric acid, $MnSO_4$ 40 g; Anthracene, 200 g; Anode, stationary — 3.7 dm² effective area.

Expt. No.	*Cell voltage (volts)*	*Current strength (amp)*	*Current density (amp/dm²)*	*Electricity passed (Amp-hr)*	*Anthraquinone formed (g)*	*Duration (hrs)*	*Current efficiency (%)*	*Yield (%)*	*Energy consumption (Kwh/kg)*	*M.P. of product (°C)*
31	4	15	4	362	224	34.13	47.7	95.8	6.46	282
32	3	7.5	4	365	225	48.66	49.0	96	5.61	282

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