

LETTERS TO THE EDITOR

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ELECTROLYTIC REACTIONS ON POROUS CARBON ANODES—PART I: The Preparation of P-Benzoquinone by the Oxidation of Benzene

p-BENZOQUINONE is largely used in the dye-stuff industry, in the preparation of hydroquinone, and in many processes of synthetic organic chemistry. It is mostly prepared by the oxidation of aniline by chromic acid. Its electrolytic preparation was attempted by Inoue and Shikata¹ who used lead peroxide as anode, and claimed a current efficiency of 81.5 per cent. Their results could not be confirmed by Seyewetz and Miodon² who obtained under identical conditions a current efficiency not exceeding 26 per cent. The latter workers obtained a current efficiency of 65 per cent., using lead peroxide as anode, and a bath containing 25 per cent. H₂SO₄, 33 per cent. CH₃COOH and 1.5 per cent. PbSO₄. The method, however, has not found any use in industry.

The advantages of using a thick-walled porous carbon tube closed at the bottom as anode are the following:—

- (1) It is cheap and chemically inert under ordinary current densities.
- (2) Catalytic materials which help anodic reactions can be easily deposited on the pores.
- (3) It can function as a wick for the passage of benzene through the pores to the active surface of the anode and thus eliminate the need for vigorous stirring which is essential for high yields of p-benzoquinone according to Seyewetz, *et al.*

Thick-walled porous carbon tubes were soaked in solutions having different concentrations of potassium ferricyanide, taken out from the bath and the adhering solution wiped off.

The tubes were then dried in an oven, and used as anodes. The electrolytic bath was composed of 2 per cent. sulphuric acid containing as catalyst, potassium ferricyanide of the same concentration as was used for impregnating the carbon anode.

Under certain conditions, a current efficiency of 51 per cent. in the electrolytic conversion of benzene to p-benzoquinone has been obtained.

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1. Inoue and Shikata, *J. Chem. Ind. Japan*, 1921 **24**, 567. 2. Seyewetz and Miodon, *Bull. Soc. Chim.*, 1923, **33**, 449.

ELECTROLYTIC REACTIONS ON POROUS CARBON ANODES—PART II: The Preparation of Chlorobenzene from Benzene

CHLOROBENZENE is now extensively used in industries for the manufacture of phenol, aniline, D.D.T., etc., and as a solvent. The well-known chemical method for the production of chlorobenzene is the chlorination of benzene in the liquid phase. The reaction is exothermic and needs careful control of temperature.

Researches on electrolytic chlorination of benzene have been fairly extensive. The latest is that of Croco and Lowy¹ who obtained with vigorous stirring (350 r.p.m.) a current efficiency of 75 per cent. using graphite anode. In our experiments stirring was eliminated, benzene was made to flow through the pores

of the anode by gravity and recycled through the anode for maximum advantage. The bath was composed of a solution of monochloroacetic acid in concentrated hydrochloric acid and could be used continuously for a series of experiments.

Using iodine, ferric chloride, and cyanuric acid as catalysts respectively, current efficiencies of 33 per cent., 68 per cent. and 89 per cent. respectively were obtained at a current density of 0.026 amp. per square cm. at 38° C.

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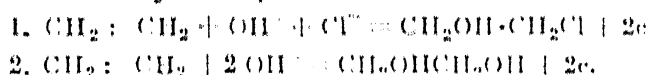
1. Croco and Lowy, *Trans. Electrochem. Soc.*, 1926, 50, 315.

ELECTROLYTIC REACTIONS ON POROUS CARBON ANODES PART III:

The Preparation of Ethylene Chlorhydrin and Ethylene Glycol from Ethylene

ETHYLENECHLORHYDRIN and ethyleneglycol are largely used as industrial solvents in the drug industry. The methods of preparation are based on the reaction between ethylene and hypochlorous acid formed by passing gaseous chlorine into water or by the action of boric acid on a hypochlorite solution. As regards their preparation by electrochemical methods, only three references could be traced.¹

It has been found that ethylene on electrolytic oxidation on a porous carbon tube as anode in an electrolytic bath of sodium chloride, produces both chlorhydrin and glycol, the yield of each depending on experimental conditions. For example, working with a solution containing 10 per cent. sodium chloride at a flow rate of ethylene of 57 c.c. per hour per sq. cm. of anode surface, and a current density of 0.023 amp. per sq. cm., the current efficiency calculated on the basis of ethylenechlorhydrin has been found to be 91 per cent. at 1° C. and 1.1 per cent. at 91° C.; and calculated on the basis of glycol has been found under identical conditions to be 5.4 per cent. at 1° C. and 16.5 per cent. at 91° C. The reactions may be represented as follows:—



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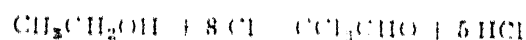
1. *B.P.*, 1916, 140, 831; *U.S.P.*, 1918, 125, 3615; *U.S.P.*, 1919, 1, 308, 797.

ELECTROLYTIC REACTIONS ON POROUS CARBON ANODES.—PART IV:

Preparation of Chloral from Alcohol

CHLORAL is now an important intermediate in the manufacture of D.D.T. Chloral alcoholate obtained by the reaction of dry chlorine with dry alcohol is converted into chloral by sulphuric acid. Koidzumi¹ has done some work on the electrolytic preparation of chloral.

In our experiments the bath was composed of a concentrated solution of sodium chloride in a copper vessel which acted as a cathode. As the alcohol was gradually introduced into the anode compartment through the porous carbon anode it reacted according to the equation:—



The experiments were carried out at 100° C. so that the chloral formed distilled off immediately and was thereby removed from further anodic attack. It was found, that besides chloral and chloral alcoholate, other products like monochloroacetic acid, ethyl acetate, monochloroacetaldehyde hydrate and alcoholate were obtained as by-products; the yields depending on experimental conditions.

Working with a saturated solution of sodium chloride maintained at a temperature of 100° C., at a current density of 0.04 amp./sq. cm. and using porous carbon impregnated with 6.5 per cent. by weight of cyanuric acid, the current efficiency calculated on the basis of chloral has been found to be 33.4 per cent.

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1. Koidzumi, *Mem. Coll. Sci. Kyoto*, 1925, 8, 155.

NOTE ON THE ESTIMATION OF CHROMIUM IN CHROMITE ORES

CHROMIUM is generally estimated in chromite ores by fusing the chromite with sodium peroxide in a nickel or a porcelain crucible. Ordinarily a nickel crucible can stand 5-6 peroxide fusions while some of the porcelain crucibles could hardly stand two fusions. Added to this, the nickel peroxide formed during fusion requires long boiling before it is completely dissolved in sulphuric acid. The chief constituent that has to be analyzed in the chromite ore is the chromium oxide (Cr_2O_3); sometimes iron oxide (Fe_2O_3) is also wanted. Silica is rarely required. In view of the scarcity and high cost of the nickel crucibles, the following simple method has been standardised employing a glass test tube for the peroxide fusion.

Sodium peroxide (1-2 g.) is introduced into a dry stout-walled test tube and finely divided