

THE OXIDATION OF BENZENE USING ANODICALLY GENERATED ARGENTIC SILVER IONS

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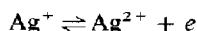
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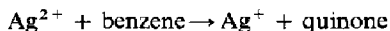
Abstract—The production of *p*-benzoquinone by the oxidation of benzene with *in situ* generated argentic silver ions in aqueous nitric acid is investigated. Parameters varied are electrode potential and current density, and concentration of argentous silver and nitric acid. Current efficiencies with respect to quinone are found to range from 55 to 30%, and corresponding chemical yields from 40 to 25%.

INTRODUCTION

The work described in the present paper deals with the oxidation of benzene to *p*-benzoquinone with argentic silver generated *in situ* at an anode dipping into an anolyte saturated with benzene. The preparation of quinone in this manner involves two main steps: an electrochemical step—the anodic formation of argentic silver



and a chemical step—the reaction of the oxidising cation with benzene



Syber[1] has oxidised benzene with argentic silver (as the oxide Ag₂O, dissolved in an acid solution) by simply mixing the two reacting solutions. He concluded that a strong oxidant could be made selective in its action by the proper choice of reaction conditions. For example with Ag₂O in 6 M perchloric and nitric acids at 10°C, quinone was obtained from benzene in 33% chemical yield. Fleischmann, Pletcher and Rafinski[2] also produced quinone from benzene by oxidation with argentic ions, which in their case were generated electrochemically *in situ*, current efficiencies of more than 30% being achieved.

The present work uses the same system and tries to optimise conditions, both for the formation of the higher valency argentic ion, and the chemical oxidation of benzene to quinone in the same solution, taking into account the effects of applied electrode potential, argentous silver and nitric acid concentrations.

EXPERIMENTAL

(Further detail on equipment and procedure can be found in reference 3.)

Instrumentation. Current was supplied either by a Chemical Electronics potentiostat, type 50V/20A, or a Farnell stabilised power supply unit L30E. The

number of coulombs passed were indicated by a permanent magnet *dc* motor integrator[4].

Electrodes. Two types of anode surfaces were used; smooth platinum and platinized titanium. Before determining any polarization data, the latter surface was pretreated cathodically in dilute perchloric acid at a *cd* of 5000 A m⁻² for 15 min, rinsed with distilled water, and then polarized anodically in dilute nitric acid at the same *cd* again for 15 min. Reproducibility of polarization measurements was considerably improved by this pretreatment. The cathode was platinized titanium in all cases.

Cell. A conventional H-type flange cell[5] made of glass was used. Anolyte and catholyte compartments were separated by a B.D.H. A-20 anion exchange membrane.

Chemicals. AnalaR-grade chemicals were used in most cases. A technical grade *p*-benzoquinone, obtained from B.D.H., was recrystallized from ether before use.

Analysis of products. The quinone formed was determined by measurement of the absorption spectra, of its condensation product with 2,4-dinitrophenylhydrazine in ethanolic potassium hydroxide solution at 550 millimicrons. The benzene in solution was determined by gas chromatography, while the oxygen evolved during electrolysis was measured volumetrically.

RESULTS

Polarization curves

In the potential range 1.6–1.9 V (all potential values in this paper are with respect to a saturated calomel electrode), argentic silver could be formed with high current efficiency, both on smooth platinum and platinized titanium anodes.

In the presence of benzene, however, passivation occurred on smooth platinum at low silver concentration (Fig. 1, curve 2) and a limited range of activity was exhibited at higher silver concentrations (Fig. 1, curve 3). There was no evidence of passivation on platinized titanium anodes, the more usual shape of polarization curve with a limiting current region

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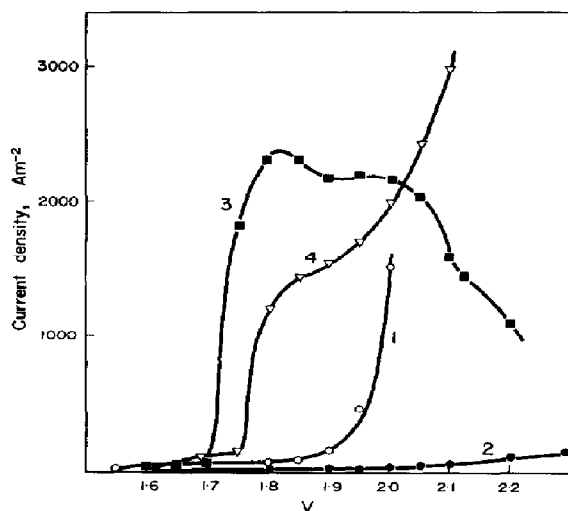


Fig. 1. Polarization curves for argentic silver in 6 M nitric acid, with and without benzene. (1) 0.01 M Ag^+ , on smooth platinum. (2) 0.01 M Ag^+ , and benzene, on smooth platinum. (3) 0.1 M Ag^+ , and benzene, on smooth platinum. (4) 0.1 M Ag^+ , and benzene, on platinized titanium.

(Fig. 1, curve 4) being obtained for all silver concentrations. Quinone was detected qualitatively in the solutions resulting from these polarization measurements.

In contrast to benzene, the presence of quinone in the argentous silver/nitric acid solutions progressively enhanced polarization currents. It would appear that an anodic reaction involving quinone is taking place.

Preparative electrolysis

Products. Qualitative analysis had already indicated the presence of quinone as a major product. Tests for any suspected phenolic by-products or intermediates proved negative, equally absent were formic acid and carbon dioxide, which would be obvious products of the decomposition of quinone or benzene in solution under the conditions of the electrolysis.

The stability of quinone. If a solution of quinone in strong nitric acid is left to stand in a closed container[3], it gradually loses its yellow colour leaving behind a faintly yellow to colourless solution smelling strongly of nitrogen dioxide. If the quinone solution originally also contains argentous silver, the former effervesces within 60 min of preparation, evolving a gas rich in nitrogen dioxide and leaving a pale yellow precipitate.

Electrolysis of quinone/silver solutions leads to additional losses of quinone, the overall rate of loss being on average almost double that observed with unelectrolysed solutions, particularly at cd above 1000 A m^{-2} . Apart from the oxygen evolved which accounted for roughly 90% of the total coulombs passed, and some nitrogen dioxide, no other gaseous products were detected from the anode compartment.

Current efficiencies. In general, electrolysis of 0.1 M argentous silver solutions in 6 M nitric acid saturated with benzene gave quinone with a current efficiency which varied from about 25 to 50%, at anode potentials below 1.9 V and cd not exceeding 3000 A m^{-2} .

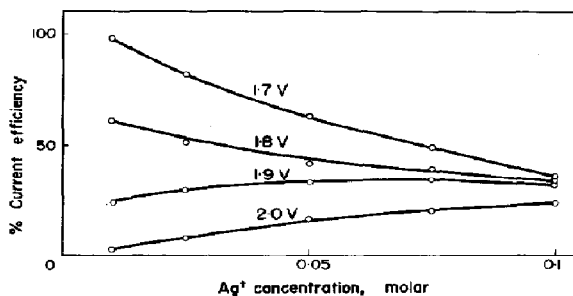


Fig. 2. Variation of current efficiency for quinone formation with Ag^+ concentration in 6 M nitric acid, at constant electrode potentials, on a platinized titanium anode.

Using controlled potential electrolysis, for any chosen electrode potential, current efficiencies tended towards a limiting value with increase in argentous silver concentration (Fig. 2). With constant current electrolysis, current efficiencies fell with increase in cd (Fig. 3).

Chemical yields. When a known amount of benzene dissolved in an aliquot of argentous nitrate solution in 6 M nitric acid, is gently treated with drops of argentous silver solution prepared separately, a chemical yield for quinone of 32% is obtained. If the argentous silver solution is added quickly, instead of in drops, the chemical yield drops to an average of about 10%. Chemical yield values are, therefore, highly sensitive to the rate of introduction of argentous silver. The same is true when argentous silver is generated by electrolysis, chemical yields decreasing with increase in current density (from 40% at 500 A m^{-2} to 21% at 3000 A m^{-2}). Lowering the concentration of nitric acid to 3 M, had no significant effect on chemical yields.

DISCUSSION

The present work was undertaken with basically two aims in mind. Firstly to get some general information on the oxidation of benzene by means of metallic redox systems, and secondly to see whether a particular set of conditions could form the basis of an industrial process for producing *p*-benzoquinone.

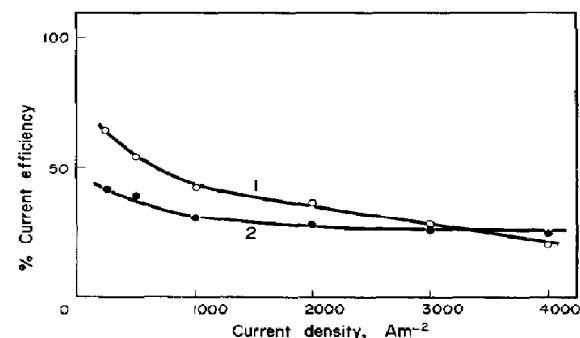


Fig. 3. Variation of current efficiency for quinone formation with cd , at constant current on a platinized titanium anode. (1) 0.1 M Ag^+ , 6 M nitric acid. (2) 0.1 M Ag^+ , 3 M nitric acid.

Considering first current efficiencies, one should note that only for very dilute Ag^+ did the quinone obtained apparently account for much more than half the current passed. Only part of the discrepancy can be due to a reaction between argentic silver and water, since for reasonable Ag^+ concentrations the combined current efficiencies for quinone and oxygen never exceeded 80%. The remaining current loss could presumably be a consequence of the destruction of quinone by silver and nitric acid, mentioned already under the heading of results.

Turning now to the chemical yield of quinone (40–25%) at cd of 500–2000 A m^{-2} , the one unidentified by-product cannot account for these relatively low values. Destruction of the quinone would appear to be the most likely cause for the low chemical yields.

A costing[3] based on a simplified flowsheet of a plant for producing quinone with the use of a silver redox system resulted in some interesting conclusions. Capital costs at over 40% represented by far the greatest proportion of the total production costs. Chemicals, in spite of the low chemical yield and an assumed loss of 50% of the silver, amounted to only 10%. A major reason for this high capital cost is the expensive electrode materials. Hence an improvement in current efficiency would reduce cell costs, which form a significant proportion of the total capital costs.

An increase in current efficiency could presumably be achieved by minimizing the residence time of quinone in the reaction mixture. Even then the best that could be expected would be gain of 20%, since as we have seen, 30% of current loss can be accounted for by the volume of oxygen evolved.

A possible serious obstacle to any successful process development is the transport of silver through the diaphragm and subsequent deposition on it. The difficulty is not so much the loss of silver, as the need for frequent diaphragm replacement. Use of a different ion exchange membrane might minimize this problem. It is clear, that although a cost estimate looks promising a number of difficulties would have to be solved before any large scale work could be recommended.

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