

Catalytic Synthesis of Hydroquinone by Using Rh on Al₂O₃ Via Different Rout

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To cite this article:

Ved Prakash Singh. Catalytic Synthesis of Hydroquinone by Using Rh on Al₂O₃ Via Different Rout. *American Journal of Optics and Photonics*. Vol. 3, No. 5, 2015, pp. 85-88. doi: 10.11648/j.ajop.20150305.15

Abstract: The catalytic synthesis of hydroquinone utilize benzene as the starting material. The manufacture of hydroquinone by oxidation of phenol and 1,2-diisopropylbenzene. The first route begin with Friedel-Crafts alkylation of petroleum-derived benzene to afford cumene. Subsequent Hock-type, air oxidation of the cumene leads to formation of acetone and phenol. The phenol is oxidized by using 70% hydrogen peroxide either in the presence of transition metal or in formic acid solution where formic acid is the actual oxidant. The generated catechol and hydroquinone mixture is separated into its pure components by distillations. The second synthesis way, which is also manufactured, is the reaction with propene and benzene to 1,4-diisopropylbenzene, which reacts afterwards to the hydroquinone. Nevertheless there are more than this two synthetic routes benzene reacts to nitrobenzene by using HNO₃ and H₂SO₄ and after that to the corresponding aniline. Next, benzoquinone is synthesized by a route employing stoichiometric amounts of MnO₂ to oxidize aniline, followed by iron catalyzed reduction to the corresponding hydroquinone. While benzene is a volatile carcinogen derived from non-renewable fossil fuel feed stocks, an alternative way to hydroquinone has been elaborated. Glucose is nonvolatile, nontoxic, and derived from renewable plant polysaccharides and plays an important role for these benzene free 3-dehydroshikimic acid (DHS). Shikimic acid as well as quinic acid are known for the hydroquinone Synthesis. In this work the starting material for the hydroquinone synthesis using catalyzed by Rh/Al₂O₃, Rh/C, Pt/C, or Pd/c. The Rh on Al₂O₃ catalyst showed the best results (59% yield).

Keywords: Benzene, Phenol, Catechol, 1,2-Diisopropylbenzene, 1,4-Diisopropylbenzene, D-glucose

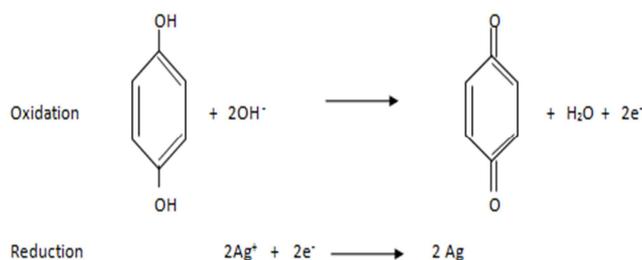
1. Introduction

Hydroquinone is white, odourless, crystalline solids with an extremely low vapor pressure; it is moderately soluble in water and high soluble in alcohol. In the presence of water, hydroquinone can slowly oxidized to quinone, which more volatile. Hydroquinone occurs naturally as a glucose ether (commonly known as arbutin) in the many plants and fruit, coffee and wheat products. Hydroquinone is found in common foods. Hydroquinone has a variety of applications. For example, it can be used in medical applications, as monomer inhibitors, for making dyes and pigments, as agricultural chemicals and so on. Hydroquinone has used for more than 100 years as a developer for black and white film including X-ray film. It is also used as raw material in the production of antioxidant for rubber, food grade antioxidants, and liquid-crystal polymers as a polymerization inhibitor for vinylacetate and acrylic monomers and a topical skin-lightening agent. Some applications and the important roles

of the hydroquinone are discussed here more in detail.

2. Application

i) Photography



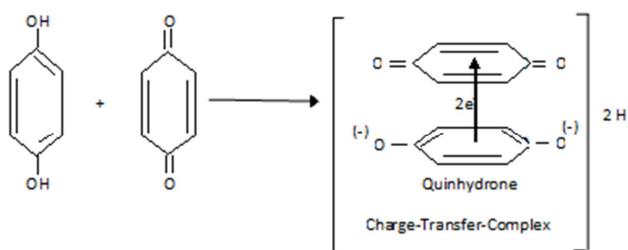
Scheme 1. Reactions during the photography.

Hydroquinone is a dihydroxybenzene and can easily be oxidized to quinone. This reducing effect is exploited in the photography. During the expose the small silver halide grains which are suspended in the photosensitive layer accumulate

development nucleus. The developer (hydroquinone) attacks at the nucleus and reduces the silver ions to black silver metallic. During the fixation the unexposed silverhalide grains are usually extracted with sodium thiosulphate, to make the left layer light-resistant (Scheme 1)

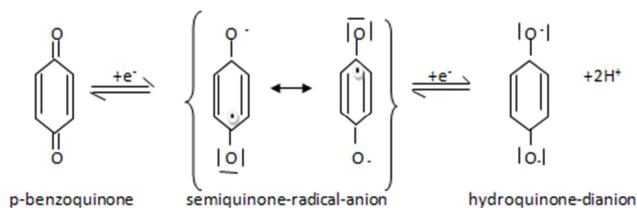
ii) Charge transfer complex

The reduction of 1,4-benzoquinone (yellow) to hydroquinone (colorless) develops a reactive intermediate the so called quinhydrone (dark green/brown). It can also be obtained by mixing equivalent quantities of p-benzoquinone and hydroquinone. In the presence of light, an electron is transferred from hydroquinone (donor) to p-benzoquinone (acceptor) giving the quinhydrone the very characteristic purple color. 1:1-adducts with this property are called "charge transfer complexes" (CT-complex) or "donor-acceptor-complex" (Scheme 2). [1] Charge-Transfer-Complex.



Scheme 2. Charge transfer complex.

The +M-effect of the two OH groups of the hydroquinone increased the electron density in the aromatic six-membered ring, so it can act as electron rich donor. The benzoquinone is the acceptor, his six-membered ring show an electron deficiency due to the -I-effect of the two oxygen substituent.



Scheme 3. Semiquinone-radical-anion.

The interaction of π -electrons leads to a facilitated excitability by electromagnetic radiation. For this reason all CT-complexes show demonstrative staining. Thereby, the electron exchange takes place in two steps over the detectable resonance stabilized semiquinone radical anion (Scheme 3).

iii) Electrochemistry: quinhydrone electrode

The redox system hydroquinone / benzoquinone in the molar ratio 1:1 is used in the pH-measurements as the so called quinhydrone electrode. Thus, pH measurements in acidic and neutral solutions can be realized. It consists of a platinum plate (inert metal electrode), which dips into the saturated quinhydrone (quinone:hydroquinone, 1:1) analysis solution. [1] Here, the electrode charged to a particular potential, which is measured by a reference electrode. The electrode half-reaction is shown in equation (i) and (ii). The

electrode-potential E of this organic half cell can be described in accordance with the equation:

$$E = E^0 + 0.059 \cdot \log \frac{[C_6H_4O_2]^{1/2}}{[C_6H_4(OH)_2]^{1/2}} \quad (i)$$

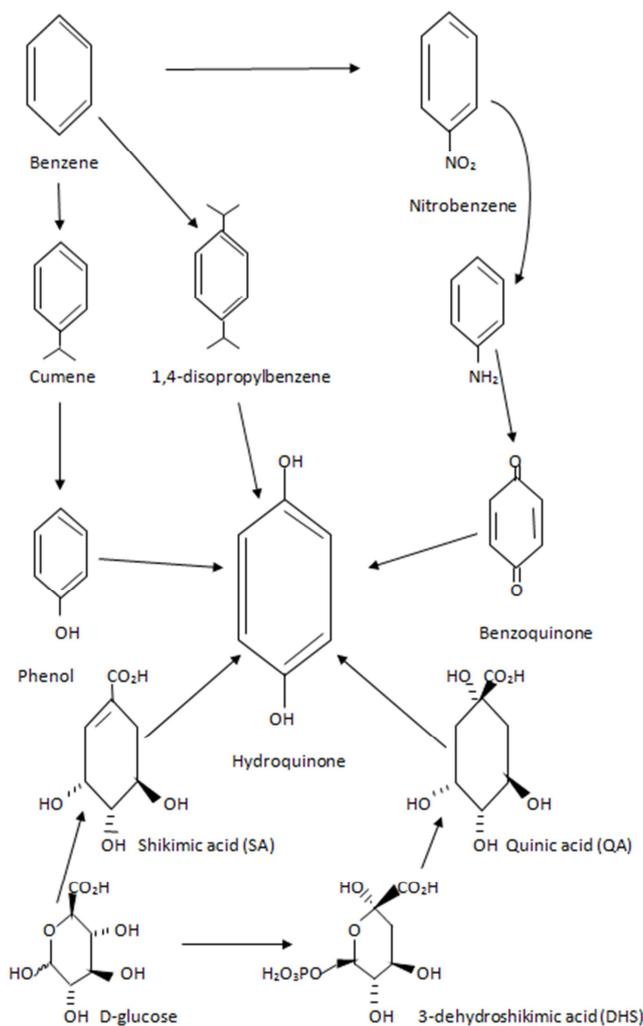
$$\text{with } \frac{[C_6H_4O_2]}{[C_6H_4(OH)_2]} = 1$$

$$E = E^0 + 0.059 \cdot \log[H^+] \quad (ii)$$

Equation(i): Electrode potential of the quinhydrone electrode.

The equation allows a fast and easy determination of the hydrogen ion concentration of any solution. However, the disadvantage of the electrode is the limitation to an acidic or neutral medium. In an alkaline solution the hydroquinone behaves like a very weak acid and absorbs hydroxyl ion, so a too high hydrogen ion concentration is determined. Additionally, the hydroquinone will be oxidized quickly to organic acids.

3. State of the Art Synthesis

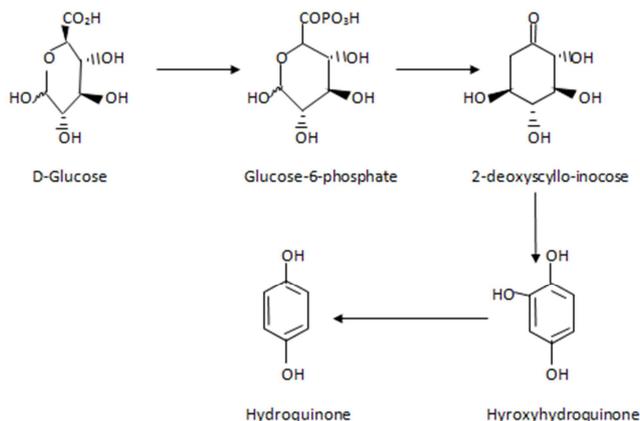


Scheme 4. Synthesis of hydroquinone.

All current routes for the synthesis of hydroquinone utilize

benzene as the starting material (Scheme 4). The manufacture of hydroquinone is now dominated by oxidation of phenol and 1,4-diisopropylbenzene.[2] The first route begins with Friedel-Crafts alkylation of petroleum-derived benzene to afford cumene. Subsequent Hock-type, air oxidation of the cumene leads to formation of acetone and phenol. Additionally this is currently the predominant method used in the production of phenol, which amounts to 5x10⁹kg annually.[3] The phenol is then oxidized using 70% hydrogen peroxide either in the presence of transition metal catalysts or in formic acid solution where formic acid is the actual oxidant. The generated catechol and hydroquinone mixture is separated into its pure components by distillations.

The second synthesis way, which is also manufactured, is the reaction with propene and benzene to 1,4-diisopropylbenzene, which reacts afterwards to the hydroquinone.[4] Nevertheless there are more than these two synthetic routes: -Benzene reacts to nitrobenzene by using HNO₃ and H₂SO₄ and after that to the corresponding aniline. Next, benzoquinone is synthesized by a route employing stoichiometric amounts of MnO₂ to oxidize aniline, followed by iron catalyzed reduction to the corresponding hydroquinone.[5] While benzene is a volatile carcinogen derived from non-renewable fossil fuel feed stocks, an alternative way to hydroquinone has been elaborated (Scheme 4).[6] Glucose is nonvolatile, nontoxic, and derived from renewable plant polysaccharides and plays an important role for these benzene free routes. From Glucose Escheria coli produce shikimic acid (SA), quinic acid (QA) and 3-dehydroshikimic acid (DHS).[7] Shikimic acid as well as quinic acid are known for the hydroquinone synthesis (Scheme 4). In 1995 the manufacture of hydroquinone and catechol has been elaborated that utilize D-glucose as the starting material and biocatalysts, a genetically modified microbe, Escheria coli.[8] Here the shikimic acid was the precursor for the quinones. Furthermore the synthesis of hydroquinone by an alternative benzene free route was published in 1838. Woskresensky synthesized the quinone from quinic acid.[9] In 1992 Drahts et al. reported about the production of quinic acid from glucose with Escheria coli.[10] They also published the oxidation of quinic acid with stoichiometric amounts of MnO₂ to benzo- and hydroquinone in low to modest yield. Next Ran and co-workers developed a new catalytic route from quinic acid to hydroquinone.[11] They used stoichiometric amounts of NaOCl, (NH₄)₂Ce(SO₄)₃, V₂O₅ or catalytic quantities of Ag₃PO₄/K₂S₂O₈ to afford 74% to 91% yield. One year later Hansen and Frost published a synthesis of 2-deoxy-scyllo-inosose from glucose which reacts to hydroxyhydroquinone (Scheme 5).[12] The latter is the starting material for the hydroquinone synthesis catalyzed by Rh/Al₂O₃, Rh/C, Pt/C, or Pd/C. The Rh on Al₂O₃ catalyst showed the best results (59% yield), whereas the Pd on carbon showed less activity (18% yield).



Scheme 5. Synthesis of hydroquinone, a benzene free route.

4. Conclusion

The rhodium catalyzed process generated an environmentally benign method. The latter is the starting material Benzene reacts to nitrobenzene by using HNO₃ and H₂SO₄ and after that to the corresponding aniline. Next, benzoquinone is synthesized by a route employing stoichiometric amounts of MnO₂ to oxidize aniline, followed by iron catalyzed reduction to the corresponding hydroquinone. While benzene is a volatile carcinogen derived from non-renewable fossil fuel feed stocks, an alternative way to hydroquinone has been elaborated. Glucose is nonvolatile, nontoxic, and derived from renewable plant polysaccharides and plays an important role for these benzene free routes. From Glucose Escheria coli produce shikimic acid (SA), quinic acid (QA) and 3-dehydroshikimic acid (DHS). Shikimic acid as well as quinic acid are known for the hydroquinone synthesis. for the hydroquinone synthesis catalyzed by Rh/Al₂O₃, Rh/C, Pt/C, or Pd/C. The Rh on Al₂O₃ catalyst showed the best results (59% yield), whereas the Pd on carbon showed less activity (17% yield).

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