

Mechanisms of molecular product and persistent radical formation from the pyrolysis of hydroquinone

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Abstract

Hydroquinone is considered to be one of the major, potential molecular precursors for semiquinone-type radicals in the combustion of complex polymeric and oligomeric structures contained in biomass materials. Comprehensive product yield determinations from the high-temperature, gas-phase pyrolysis of hydroquinone in two operational modes (rich and lean hydrogen conditions) are reported at a reaction time of 2.0 s over a temperature range of 250–1000 °C. Below 500 °C, *p*-benzoquinone is the dominant product, while at temperatures above 650 °C other products including phenol, benzene, styrene, indene, naphthalene, biphenylene, phenylethyne, dibenzofuran and dibenzo-*p*-dioxin are formed. Hydrogen-rich conditions initially inhibit hydroquinone decomposition (below 500 °C) but promote product formation at higher temperatures. The decomposition process apparently proceeds via formation of a resonance stabilized *p*-semiquinone radical. Detailed mechanisms of formation of stable molecular species as well as stable radicals are proposed. © 2007 Elsevier Ltd. All rights reserved.

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1. Introduction

Hydroquinone, HQ, (1, 4-dihydroxybenzene or 1,4-benzenediol) and its simple derivatives are well documented products of the combustion and pyrolysis of many types of biomass, including tobacco (Visser et al., 1985; Lee et al., 1999). It is thought to originate from thermal degradation of lignin and other polymeric plant materials that usually contain aryl ether and aryl alcohol linkages (Simoneit, 2002; Font et al., 2003).

Inhalation of HQ has been shown to induce coughing, burning sensations, labored breathing in humans (Bilimoria, 1975; Leanderson and Tagesson, 1992) as well as reduced bone marrow and corneal damage in mice (Bilimoria, 1975; Leanderson and Tagesson, 1992). However, the overriding concern with HQ in combustion and pyrolysis is its degradation to produce persistent, semiquinone-type free radicals and other toxic by-products.

It is known that the pyrolysis of HQ leads to the formation of *p*-benzoquinone and phenol (Sakai and Hattori, 1976; Khachatryan et al., 2006) as well as a number of other aromatic and polycyclic aromatic hydrocarbon products (Ledesma et al., 2003; Marsh et al., 2004). In addition, studies of burning cigarettes strongly suggest that HQ is a precursor for formation of highly stable semiquinone-type radicals (Pryor et al., 1983; Zang et al., 1995). These types of radicals are strong reducing agents that can induce the formation of reactive oxygen species (ROS), super-oxide and hydroxyl radicals, under physiological conditions that are suspected to induce cancer, heart disease and lung disease (Pryor et al., 1983, 1998; Leanderson and Tagesson, 1992; Dellinger et al., 2001; Squadrito et al., 2001; Hirakawa et al., 2002).

This manuscript presents the results of studies of product formation from the pyrolysis of HQ over the temperature range of 250–1000 °C as a pure compound and under hydrogen-rich conditions. We develop a mechanism that explains the observed products and discuss its potential role in the formation of environmentally persistent,

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semiquinone-type free radicals and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F).

2. Methods and materials

All experiments were performed using a high-temperature, flow reactor analytical system, referred to in the archival literature as the System for Thermal Diagnostic Studies (STDS) (Rubey and Grant, 1988; Striebich and Rubey, 1990; Striebich et al., 1991). The STDS consists of a high-temperature, fused silica flow-reactor (1 cm i.d.) contained inside a high-temperature furnace (maximum operating temperature of 1100 °C). The furnace and transfer lines are housed inside a GC oven (Varian, CP 3800) controlled at constant temperature of 200 °C to facilitate transport of gas-phase reactants and products. The reactor effluent is transported through a heated, temperature-controlled transfer line (deactivated, silica-lined, stainless steel tube) where it is trapped cryogenically at the head of the capillary column at –60 °C of a GC–MS system (Varian, Saturn 2000). The pressure inside the flow reactor is typically maintained at 101 ± 15 kPa.

HQ was pyrolyzed in two reaction atmospheres: (a) pure HQ in a helium gas carrier and (b) HQ in the presence of a hydrogen-rich source (isopropyl alcohol, which was used to dissolve HQ) in a helium gas carrier. The latter case more closely simulates the reaction atmosphere in a typical combustion/thermal process where other fuel components contribute to the overall hydrogen concentration.

For the studies of pure HQ, a Chromatoprobe® (Varian) was used to introduce HQ to the system. A Chromatoprobe® is a solid phase vaporizer that inserts into injection port of a reactor part GC system. It has a precise programmable temperature controller to maintain constant concentration of vapors from solid samples. Pure solid samples of HQ were placed into the quartz micro-vial at the bottom of the chromatoprobe shaft. The temperature of injection in the chromatoprobe was programmed in order to maintain a gas-phase concentration of reagents of 35 ppm.

For the studies in the presence of isopropyl alcohol, 1 µL of 1 M solution of HQ was injected into a helium gas stream. A digital syringe pump (Kd Scientific 100) was used to maintain a constant gas-phase concentration of 60 ppm HQ inside the reactor. Additionally, the injection port was maintained at a temperature of 180 °C to vaporize all of the HQ-containing solution.

In both cases, the carrier gas (helium) flow rate was varied over the operating temperature range of 250–1000 °C to maintain a reactor residence time of 2.0 s. The temperature of the surrounding GC oven and all transfer lines were maintained at 200 °C, which was high enough to ensure transport of gas-phase reactants and products without condensation. The thermal degradation products were swept through a heated transfer line (1.0 m long, 0.5 mm i.d., 200 °C) into a GC–MS (Varian Saturn 2000) equipped with

a 30 m, 0.25 mm i.d., 0.25 µm film thickness capillary column (Restek Rtx®-5MS). Initially, all the products were trapped at the head of capillary column at the temperature of –60 °C, followed by temperature programmed ramping of the column from –60 to 300 °C at 15 °C min^{–1}. Separated products with molecular weights from 40 to 650 amu were analyzed with a mass spectrometer (Varian, Saturn 2000) operating in the full-scan mode. The mass-spectral library (NIST 98 version 1.6 d) was used to identify the products.

Quantizations of reactants and products were performed based on the calibration curves using analytical standards (Sigma–Aldrich). Calibration was based on the area counts of the peaks on the chromatogram. The yields of the products were calculated using a following formula: $Y = (P/P_o) \times 100$, where Y (%) is percent yield, P (mol) is the total mole of the particular product formed, and P_o (mol) is the initial mole of HQ injected into the system.

The total carbon balance of the reaction was not performed due to the method limitations, i.e. the products with the mass lower than 60 amu are not resolvable using the GC column used to separate the higher molecular weight products of interest in this study.

3. Results

The thermal degradation behavior and product formation from the pyrolysis of HQ, with hydrogen-rich and hydrogen-lean conditions, is presented in Fig. 1a and b, respectively. In both cases, the thermal degradation of HQ was initiated at 250 °C and gradually increased with temperature. The thermal degradation of HQ under hydrogen-rich conditions increased rapidly at 700 °C and HQ was completely degraded by 750 °C, while decomposition of HQ in the hydrogen-lean conditions was not complete until 800 °C. Differences in the product distribution were also observed.

3.1. Hydrogen-rich condition (with addition of isopropyl alcohol solvent)

p-Benzoquinone formation occurred immediately upon degradation of HQ at 250 °C with a maximum yield of 33% at 550 °C persisting until 750 °C. Both *p*-benzoquinone and phenol were the only observable products at low temperature below 650 °C while many products were detected above 650 °C. Phenol was formed from 550 °C to 900 °C with a maximum yield of ~2% at 700 °C and benzene was observed around 650 °C with a maximum yield of 9.5% at 900 °C. Above 700 °C, substituted aromatic by-products were formed including styrene, indene, naphthalene, biphenylene and phenylethyne with maximum yields of 15% at 850 °C, 2% at 850 °C, 2% at 925 °C, 6% at 900 °C, 2% at 950 °C, respectively. Dibenzofuran was detected in the narrow temperature range from 800 to 900 °C with maximum yield of 0.2% at 850 °C.

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