



Mechanisms of product formation from the pyrolytic thermal degradation of catechol

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ABSTRACT

Catechol has been identified as one of the most abundant organic products in tobacco smoke and a major molecular precursor for semiquinone type radicals in the combustion of biomass material. The high-temperature gas-phase pyrolysis of catechol under hydrogen-rich and hydrogen-lean conditions was studied using a fused-silica tubular flow reactor coupled to an in-line GC/MS analytical system. Thermal degradation of catechol over temperature range of 250–1000 °C with a reaction time of 2.0 s yielded a variety of products including phenol, benzene, dibenzofuran, dibenzo-*p*-dioxin, phenylethyne, styrene, indene, anthracene, naphthalene, and biphenylene. *Ortho*-benzoquinone which is typically associated with the presence of semiquinone radicals was not observed and is proposed to be the result of fast decomposition reactions that lead to a variety of other reaction products. This is in contrast to the decomposition of hydroquinone that produced *para*-benzoquinone as the major product. A detailed mechanism of the degradation pathway of catechol is proposed.

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1. Introduction

Catechol (CT) has been identified as one of the most abundant organic chemical in tobacco smoke and a product of combustion of any type of biomass (Kallianos et al., 1968; Schlotzhauer et al., 1982; Carmella et al., 1984; Dellinger et al., 2001). Catechol groups are major components of the molecular structure of lignin, which comprises the woody component of biomass materials (Hayashi and Namura, 1966; Troughton et al., 1972; Dorrestijn et al., 2000; Hays et al., 2005). Exposure to CT has been reported to induce high-blood pressure and upper respiratory tract irritation as well as kidney damage and convulsions in high-doses (Vasil'ev and Matlina, 1972; Flickinger, 1976; Sax and Lewis, 1988; Van Duursen et al., 2004). Studies of cigarette smoke suggest that CT contributes to lung cancer and DNA damage through the formation of biologically active semiquinone radicals (Pryor et al., 1983a,b; Borish et al., 1985; Leanderson and Tagesson, 1990, 1992; Bermudez et al., 1994; Li and Trush, 1994; Pryor, 1994; Stone et al., 1995; Dellinger et al., 2000; Dellinger et al., 2001; Squadrito et al., 2001). In biological systems, radicals can attack proteins and DNA that lead to their destruction and diminished capacity to carry out normal biochemical cell processes.

Thermal degradation of CT may also lead to formation of other by-products including dibenzo-*p*-dioxins with significant health

and environmental impacts. Recently, Wornat et al., reported a study of the pyrolysis of CT using GC-FID and HPLC for product analysis (Wornat et al., 2001; Ledesma et al., 2002, 2003; Marsh et al., 2004); however, the focus of their research was the formation of polycyclic aromatic hydrocarbons.

We present the results of our research on the thermal degradation of CT at a gas-phase reaction time of 2.0 s over a temperature range of 250–1000 °C using a high-temperature flow reactor equipped with an in-line GC–MS analytical system. Based on the results, we propose a mechanism for decomposition of CT and formation of organic by-products.

2. Methods and materials

The pyrolysis of CT was studied by 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 that is 35-cm long with a 1 cm inside diameter in a helical configuration. This flow reactor is contained within a high-temperature furnace with a maximum operating temperature of 1200 °C. The furnace is housed inside a GC oven (Varian, CP 3800) that is controlled at a 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) to the head of the capillary column of a GC–MS System where it is cryogenically trapped

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at $-60\text{ }^{\circ}\text{C}$. The transfer line temperature was maintained at $200\text{ }^{\circ}\text{C}$ to ensure transport of gas-phase products without thermal degradation. To prevent GC–MS column overload and damage to the detector, the reactor effluent flow splits in a 1 to 4 ratio. The pressure was maintained at $101 \pm 15\text{ kPa}$ inside the flow reactor. All experiments were performed at a reactor residence time of 2.0 s.

CT was pyrolyzed under two reaction conditions: (A) pure CT vapors in a helium gas carrier and; (B) CT in the presence of hydrogen-rich source (isopropyl alcohol that was used to dissolve CT) in a helium gas carrier. The latter case more closely simulates the reaction conditions in a typical combustion/thermal processes where other fuel components contribute to the overall hydrogen concentration.

For the pyrolysis studies of pure CT, a Chromatoprobe[®] (Varian) (a solid-phase vaporizer inserted into injection port of the GC portion of the thermal reactor) was used to vaporize CT for introduction into the flow reactor carrier gas stream. Pure solid samples of CT were placed into a quartz micro-vial at the bottom of the chromatoprobe shaft. The chromatoprobe temperature was maintained at $80\text{ }^{\circ}\text{C}$ which resulted in a constant gas-phase concentration of CT of 35 ppm.

For the pyrolysis studies of CT in the presence of isopropyl alcohol, a digital syringe pump (Kd Scientific 100) was used to inject $1\text{ }\mu\text{l}$ of a 1 M solution into the helium carrier gas stream to maintain a constant gas-phase concentration of 60 ppm CT inside the reactor. The injection port was maintained at a temperature of $180\text{ }^{\circ}\text{C}$ to vaporize all of the CT solution.

The thermal degradation products were swept through the heated transfer line 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). All the products were trapped cryogenically at the head of capillary column at a temperature of $-60\text{ }^{\circ}\text{C}$, followed by temperature programmed ramping of the column from -60 to $300\text{ }^{\circ}\text{C}$ at $15\text{ }^{\circ}\text{C}/\text{min}$. Separated products with molecular weights from 40 to 650 amu were analyzed with a Mass Spectrometer operating in a full-scan mode. The mass-spectral library (NIST 98 version 1.6d) was used to identify the products. Quantification of reactants and products was 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 the following formula: $Y = P/P_0 \times 100$, where: Y is percent yield, P is the concentration of the particular product (or the CT reactant) in moles, and P_0 is the number of moles of CT injected into the reactor.

3. Results

The product distribution from the thermal degradation of CT under hydrogen-lean and -rich conditions varied significantly. The yields of all products were lower under hydrogen-lean than hydrogen-rich conditions.

3.1. Hydrogen-rich condition: CT in the presence of isopropyl alcohol

Fig. 1 A presents the temperature dependence of the percent yields of product formation from gas-phase pyrolysis of CT under hydrogen-rich conditions. The thermal degradation of CT initiates at $250\text{ }^{\circ}\text{C}$ and rapidly increases at $550\text{ }^{\circ}\text{C}$. At $\sim 750\text{ }^{\circ}\text{C}$, the CT concentration dropped to below the detection limit. In contrast to the formation of *p*-benzoquinone from the pyrolysis of hydroquinone, the analogous formation of *o*-benzoquinone from CT was not observed (Truong et al., in press).

Phenol was formed in the temperature range of $600\text{--}900\text{ }^{\circ}\text{C}$ reaching a maximum yield of 1.8% at $750\text{ }^{\circ}\text{C}$. Benzene was detected from 650 to $1000\text{ }^{\circ}\text{C}$ with a relatively constant high-yield of 6.5%

from 850 to $950\text{ }^{\circ}\text{C}$. At $650\text{ }^{\circ}\text{C}$, dioxin-type products began to form. Dibenzo-*p*-dioxin (DD) was observed from 650 to $800\text{ }^{\circ}\text{C}$ with a maximum yield of 0.7% at $700\text{ }^{\circ}\text{C}$, while dibenzofuran (DF) was detected over the temperature range of $650\text{--}1000\text{ }^{\circ}\text{C}$ with a maximum yield of 3.5% at $750\text{ }^{\circ}\text{C}$.

Above $650\text{ }^{\circ}\text{C}$, polycyclic aromatic hydrocarbons (PAHs) and substituted aromatic products were detected. These by-products were styrene, indene, naphthalene, biphenylene, and phenylethyne with maximum yields of 8.2% at $900\text{ }^{\circ}\text{C}$, 1.2% at $850\text{ }^{\circ}\text{C}$, 1.4% at $950\text{ }^{\circ}\text{C}$, 3.4% at $950\text{ }^{\circ}\text{C}$, and 0.80% at $950\text{ }^{\circ}\text{C}$, respectively. They are formed as a result of the CT fragmentation into C2, C3 and C4 products, followed by the gas-phase, molecular growth reactions (Melius et al., 1996; Mulholland et al., 2000; Wang et al., 2006).

3.2. Hydrogen-lean conditions: pure CT

The temperature dependence and product yields from the gas-phase pyrolysis of CT under hydrogen-lean conditions (pure CT, without the presence of isopropyl alcohol solvent) are presented in Fig. 1B. The decomposition of CT initiated at $250\text{ }^{\circ}\text{C}$ increased slightly with temperature until $850\text{ }^{\circ}\text{C}$ where a rapid decomposition to below detectable levels was observed. As was the case for hydrogen-rich conditions, *o*-benzoquinone was not detected.

The only observable product at lower temperatures was phenol from 550 to $850\text{ }^{\circ}\text{C}$, which achieved a maximum yield of $\sim 0.2\%$ at $700\text{ }^{\circ}\text{C}$. DF was the only observable dioxin-like product with a maximum yield of $\sim 0.3\%$ at $900\text{ }^{\circ}\text{C}$ (no DD was detected). Benzene was not detected until $900\text{ }^{\circ}\text{C}$ with a maximum yield of $\sim 0.3\%$ at $950\text{ }^{\circ}\text{C}$. PAH and PAH precursors were detected above $800\text{ }^{\circ}\text{C}$ including: anthracene, naphthalene, biphenylene and phenylethyne with maximum yields of $<1.0\%$ at $900\text{ }^{\circ}\text{C}$, 1.6% at $950\text{ }^{\circ}\text{C}$, 1.2% at $950\text{ }^{\circ}\text{C}$, and $<1.0\%$ at $950\text{ }^{\circ}\text{C}$, respectively.

4. Discussion

CT and hydroquinone are both dihydroxyl benzenes, with the hydroxyl groups located in *ortho*- and *para*- positions, respectively. Based on their structural similarities, similar products of their thermal degradation were expected. As we have previously reported (Truong et al., in press), the principal decomposition product of hydroquinone at low-temperatures was *p*-benzoquinone with a maximum yield of 32% at $550\text{ }^{\circ}\text{C}$. The *p*-benzoquinone forms from the sequential loss of the two phenoxyl-hydrogens via unimolecular decomposition or abstraction. The lack of *ortho*-benzoquinone in the products of thermal degradation of CT was unexpected and led us to a conclusion that the initial steps of CT decomposition must be quite different from that of hydroquinone (cf. Scheme 1).

The bond dissociation energy for the first hydroxyl hydrogen to form a semiquinone radical is large given the heats of reaction of 79.3 kcal/mol for CT and 80.8 kcal/mol for hydroquinone (Lucarini et al., 2002). The rupture of the second hydroxyl hydrogen bond is expected to be much lower because the semiquinone radical would be converted to more stable molecular species, *o*-benzoquinone and *p*-benzoquinone for CT and HQ, respectively. However, the close proximity of the two *ortho*-hydroxyl groups in CT suggest that a concerted, intra-molecular water elimination process that would result in the formation of epoxy benzene or fission of the central bond between the two vicinal hydroxyl-groups followed by tautomerization to form olefinic carbonyls may occur (cf. Scheme 1).

Either concerted pathway or carbon–carbon bond fission would account for the lack of observation of *o*-benzoquinone from the decomposition of CT. From our GC–MS analyses of the reactor effluent it did not reveal the presence of either epoxy-benzene, C2–C4 olefinic hydrocarbons, or carbonyl decomposition products.

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