

FORMATION OF DIBENZO-*P*-DIOXIN AND DIBENZOFURAN FROM CATECHOL IN RELEVANCE TO COMBUSTION OF BIOMASS

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1. Introduction

Pyrolysis of biomass constitutes a critical front in the pursuit of utilising renewable energy at a wider scale. The complex chemical and physical processes occurring during thermal treatment of biomass are in the centre of a mounting research interest. Great deal of this research aims to understand emission of pollutants from thermal utilisation of biomass.¹ The intricate chemical composition of biomass constituents makes it a daunting task to assign formation of organic pollutants to a specific chemical reaction. To overcome complexity pertinent to structure of biomass, model compounds or “surrogates” are often used to mimic characteristics of the real fuel, biomass. The most discussed compounds in this context are dihydroxylated benzenes, catechol (*o*-dihydroxybenzene and hydroquinone (*p*-dihydroxybenzene)). Catechol (CT hereafter) is a major product from the combustion of any type of biomass.² Decomposition of CT was found to form various species, including phenol, benzene, naphthalene, and polycyclic aromatic hydrocarbons.³ Dellinger’s group has thoroughly investigated thermal decomposition of CT.^{4,5} In addition to previously identified products, they found that, thermal degradation of CT leads to the formation of dibenzo-*p*-dioxin (DD) and dibenzofuran (DF). Using electro paramagnetic resonance (EPR), Khachatryan *et al.*⁵ detected the formation of *o*-semiquinone (*o*-SQ) as the most prominent initial intermediate from decomposition of the CT molecule via fission of one of its phenolic O-H bonds. Along the same line of enquiry, we have shown in a theoretical study, that main exit channel of the *o*-SQ radical is through CO/ring-contraction mechanism leading to the formation of *cyc*-C₅H₄OH radical.⁶ Based on our reported reaction constant for the latter channel, a life time of the *o*-SQ radical falls around 2200 s. The relatively long lifetime of the *o*-SQ supports its categorisation as an environment persistent free radical (EPFR).⁵ Thus, the *o*-SQ radical could serve as a building block for the formation of DD and DF. Truong *et al.* suggested a pathway for the evolution of DD and DF from pyrolysis of the CT molecule based on the well-established analogous mechanism of the chlorophenol systems.^{7,8} However, this proposed mechanism does not take into account a plausible role of the OH group in facilitating the occurrence of prominent reaction steps; most notably ring-closure reaction and initial coupling modes. In this contribution, we demonstrate, for the first time, a comprehensive mechanism for the formation of DD and DF (and their hydroxylated derivatives) from catechol. Results presented herein should provide an insight into emission of DD and DF from thermal processing of biomass.

2. Methodology

Theoretical calculations were performed with the Gaussian09 code⁹ at meta hybrid density theory functional (DFT) of M062X¹⁰ together with a moderate basis set of 6-311+g(d,p). The nature of all transition structures were verified via calculating intrinsic reaction coordinates (IRC).

3. Results and Discussions

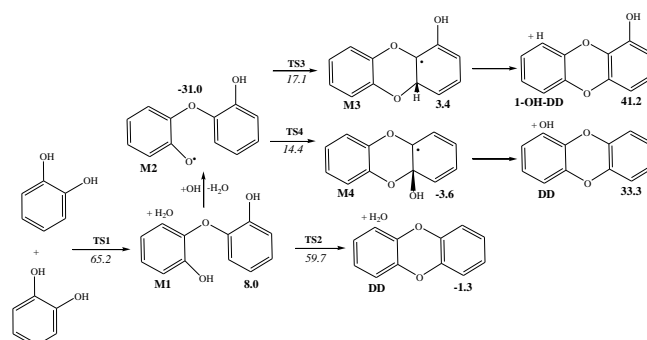
As it is the case in phenol and its substituted derivatives, the CT and its derived *o*-SQ radical could undergo three types of coupling modes, namely self-condensation of two CT molecules (CT/CT), molecule/radical combination (CT/*o*-SQ) and self-couplings of two *o*-SQ radicals (*o*-SQ/*o*-SQ).

3.1. Formation of DD from self-condensations of CT

Figure 1 depicts reaction pathways for synthesis of the DD molecule initiated by self-condensation of two CT molecules. As shown in the lowermost pathway in Figure 1, a DD molecule evolves as a result of two water elimination steps. In the first step, a 2,2'-oxydiphenol molecule (M1) forms upon attack of the hydroxyl group of

one CT molecule on the hydroxyl's H atom in the other CT molecule. In the second step, a closed-shell cyclisation reaction occurs simultaneously with the departure of a water molecule. These two steps proceed via transition structures TS1 and TS2 with calculated activation enthalpies of 65.2 kcal/mol and 59.7 kcal/mol, respectively. Enthalpic barrier of TS1 is close to a corresponding barrier for HCl elimination reaction, the opening channel in the self-condensation of two 2-chlorophenol molecules.⁷ Radical pool in the combustion media (most notably OH) could readily abstract one of the hydroxyls' H atoms in the M1 intermediate to yield the oxygen-centered radical of M2. An attachment of the phenoxy's O in the M2 intermediate at an *ortho* site bearing H and OH in the neighbouring phenol ring occurs through similar activation enthalpies of 17.1 kcal/mol (TS3) and 14.1 kcal/mol (TS4), respectively. Products from these two cyclisation reactions are M3 and M4 adducts. Loss of an H and OH from M3 and M4 intermediates yields a hydroxylated DD (1-OH-DD) and DD molecules, in that order.

Figure 1: Pathways to formation of DD and 1-OH-DD molecules from self-condensation of two CT molecules. Values in bold and italic denote reaction and activation enthalpies, respectively. All values are in kcal/mol, as calculated at 298.15 K.



3.2. Formation of DD, DF and their hydroxylated derivatives from CT/*o*-SQ coupling mode

Considering the four distinct radical sites in the *o*-SQ radical, there are 15 different possible products from combination of the *o*-SQ radical and its parent CT molecule. Herein, we demonstrate pathways for the formation of DD/DF from two important initial CT/*o*-SQ coupling products. In order to show unique branching network in the CT system, we elect to discuss pathways leading to formation of DD and DF initiated by adding of the phenoxy's O in the *o*-SQ radical to C(OH) and an *ortho* C(H) positions in the CT molecule. These pathways are shown in Figure 2 with embedded reaction and activation enthalpies pertinent to individual steps. It is anticipated that formation of DD and DF from the other CT/*o*-SQ coupling products incurs similar enthalpic profiles. Attachment of the phenoxy'O in the *o*-SQ radical to C(OH) and an *ortho* C(H) sites produces the two ether-type intermediates of M5 and M6 via endothermic reactions of 23.1 kcal/mol and 18.1 kcal/mol, respectively. These two addition reactions occur without passing over an intrinsic barrier. There are three exit corridors for M5 and M6 adducts:

- Losses of H/OH at the ether bridge either unimolecularly or through abstraction reactions operated by radicals present in the combustion media. Self-ejection of H and OH from M4 and M5 intermediates afford the hydroxylated diphenyl ethers M7 and M1; respectively, via moderate endothermicity of 20.5 and 23.0 kcal/mol, respectively.
- Cyclisations of M5 and M6 with simultaneous elimination of water molecules. Formation of the two preDD intermediates M3 and M8 via this cyclisation-type reaction requires substantial activation enthalpies of 58.0 kcal/mol (TS5) 60.1 kcal/mol (TS6), respectively. Departure of the out-of-plane H and OH in M3 and M8 afford hydroxylated DD of 1-OH-DD and DD molecules, correspondingly.

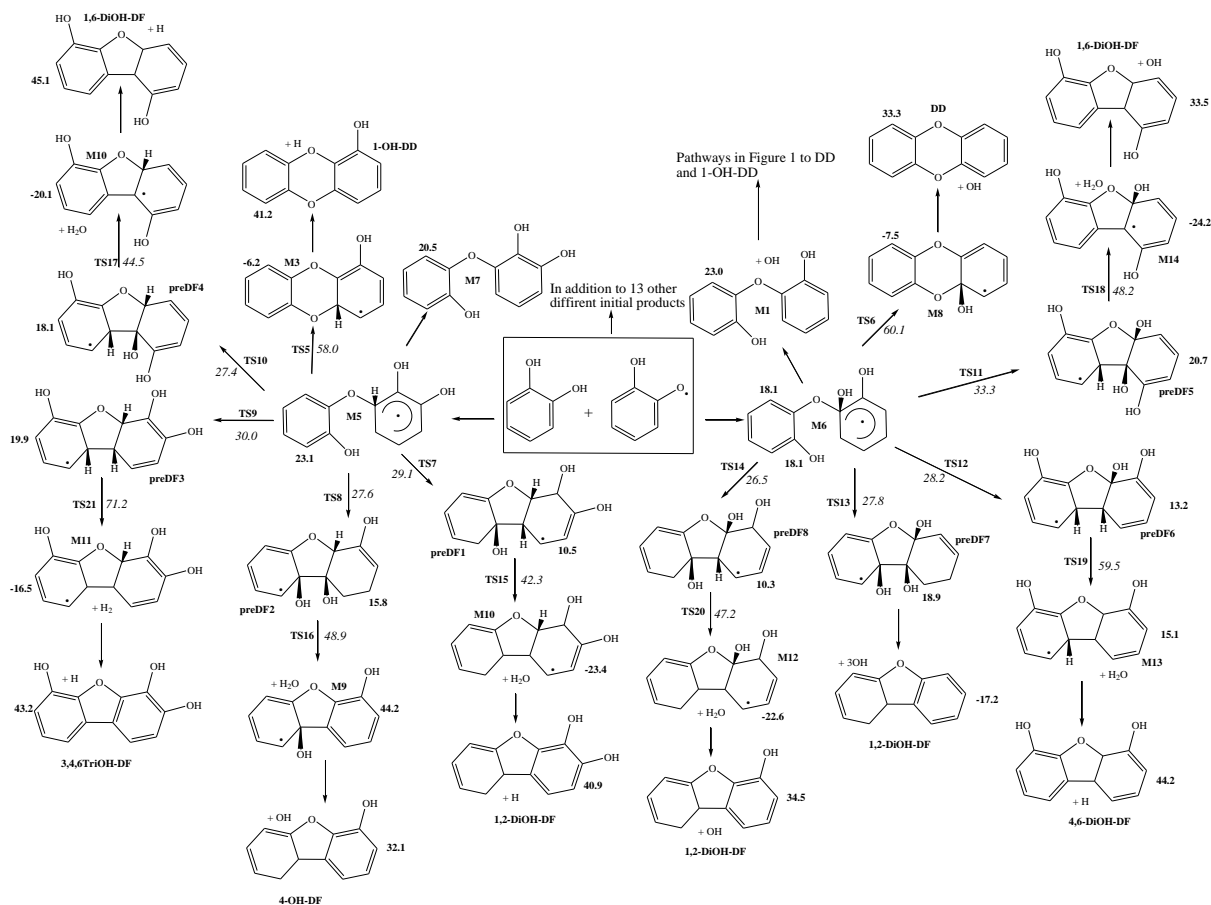
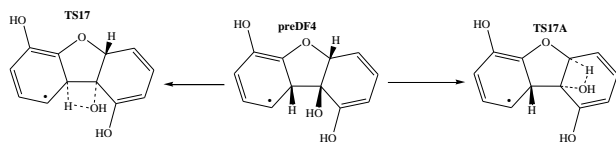


Figure 2: Pathways to products from two CT/*o*-SQ coupling species. Values in bold and italic denote reaction and activation enthalpies, respectively. All values are in kcal/mol calculated as at 298.15 K.

- C-C cross-linkages leading to formation of preDF intermediates. In each phenyl ring in M5 and M6, there exist two *ortho* potent cross-linkage sites. It follows that, there are four plausible C-C bridging-type reaction products for M5 (preDF1-preDF4) and M6 (preDF5-preDF8). Formation of these eight preDF intermediates is slightly endothermic (10.5 kcal/mol – 20.7 kcal/mol) and requires activation enthalpies in the narrow range of 26.5-33.5 kcal/mol (TS7-TS14). Figure 2 demonstrates that, DF and its hydroxylated derivatives arise from preDF intermediates via water elimination reactions (TS15-TS20), hydrogen elimination (TS21) and unimolecular loss of out-of-plane H or OH moieties.

Scheme 1



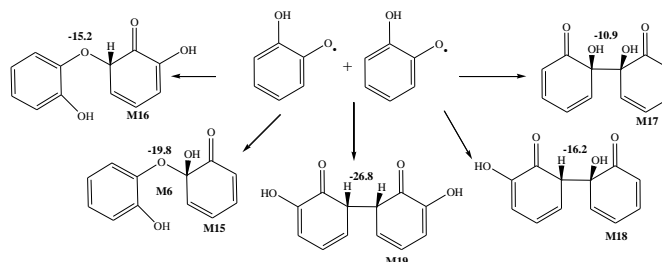
Water elimination from preDF4 and preDF8 intermediates could potentially occur via two channels, as depicted in Scheme 2 for preDF 4. Enthalpic barrier for TS17A overshoots that of TS17 by 15.9 kcal/mol. In Figure 2, we have considered the water elimination channel corresponding to the lowest enthalpic barrier. While enthalpic barriers for preDF (26.5 kcal/mol-33.5 kcal/mol) channels are significantly lower than that of preDD (58.1 kcal/mol and 60.1 kcal/mol), the loss of H (20.5 kcal/mol) and OH (23.0 kcal/mol) from the ether linkage in M5 and M6 intermediates, either unimolecularly or bimolecularly, is more preferred than channels leading to preDF.

Figure 1 portrays that unimolecular rearrangement of hydroxylated diphenyl ethers (M5 and M6) lead solely to the formation of DD/OHs-DD derivatives after loss of H/OH from their pivot carbon atoms.

3.3. Initial products from *o*-SQ/*o*-SQ combinations.

Figure 3 displays five products from these self-condensation of two *o*-SQ radicals. These products feature attachment of phenoxy's O in one *o*-SQ radical to the two *ortho* positions in the other *o*-SQ (M15 and M16), and the three plausible *ortho* C-C coupling products (M17-M19). We have chosen to study formation of these five particular intermediates because they are more relevant to generation of DF/DD than products from couplings involving *meta* and *para* sites.

Figure 3: Selected initial products *o*-SQ/*o*-SQ couplings. Values in bold and italic denote reaction and activation enthalpies, respectively. All values are in kcal/mol calculated at 298.15 K.



Formation of the dihydroxylated diketo M19 is thermodynamically more preferred than formation of the other two keto-keto adducts (M17 and M18). Likewise, attachment of the phenoxy O at an C(OH) *ortho* site incurs slightly more exothermicity than the corresponding attachment at an *ortho* C(H) site. Clearly, M15 and M16 intermediates serve as building blocks for production of DD/OHs-DF, as demonstrated in Figures 1 and 2. Formation of hydroxylated DFs from M17-M19 intermediate follows the well-established analogous mechanism in chlorophenol systems.^{7,8}

4. Concluding Remarks

This contribution presents mechanistic pathways underlying the formation of DF/DD and their hydroxylated derivatives from bimolecular reactions involving CT with *o*-SQ radical as model compounds for structural entities in biomass. Self-condensation of two CT molecules is found to afford solely DD and 1-OH-DD. Pathways to formation of DF and DF are mapped out from selected products of CT/*o*-SQ and *o*-SQ/*o*-SQ. In the former system, direct cyclisation of ether-type adducts into preDD intermediates is found to incur significantly higher activation enthalpies than C-C cross linkage reactions leading to preDF intermediates. However, loss of an H or OH from pivot carbon linkage in ether-type adducts is predicted to be associated with lower enthalpic requirements than pathways leading to formation of DF (and OHs-DF). While our theoretical modelling predicts formation of hydroxylated derivatives of DF and DF in parallel competing routes to those of DF and DD, Dellinger's group did not detect their formation. A plausible explanation for the absence of OHs-DF/DD is their predicted rapid decomposition initiated by loss of a hydroxyls' H; in an analogy to the mechanism of the thermal decomposition of phenol.

Acknowledgment

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