

The Pyrolysis Of Resorcinol: Search For Direct CO₂ Pathways

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Introduction and background

Third generation biofuels based on lignocellulosic biomass are beneficial as they prevent competition with the food chain, which makes them preferred alternatives to fossil fuels and feedstocks. However, the lignin component introduces aromatic molecules such as phenols, phenyl methyl esters and others. Similar components are often used to present solid fuels such as coal. Since pyrolysis chemistry is an integral part of any combustion model, the thermal reactions of functionalized aromatic molecules are of general interest in the search for suitable renewable sources for energy carriers. In this study, the focus is on hydroxyphenols with a particular emphasis on resorcinol. The three possible hydroxyphenol isomers are depicted in Figure 1.

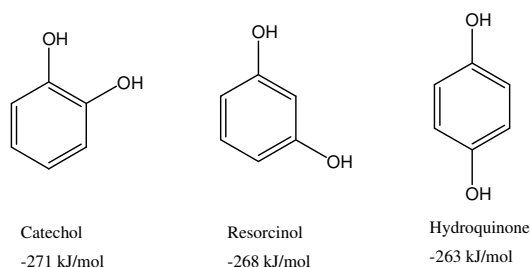


Figure 1: Structures and BAC corrected CBS-QB3 D_fH^{298} of the three hydroxyphenol isomers

A recent experimental study by Yang et al. [1] using a two-stage tubular reactor with online GC analysis, operating with residence times up to 3.6 s at 923 – 1223 K, lead to the interesting discovery that CO₂ production in the pyrolysis of resorcinol was significantly higher than that found in catechol and hydroquinone decomposition. In addition, larger yields of C₅ components were detected. The findings of Yang et al. qualitatively support previous experimental data obtained with a hyperthermal micro-tubular reactor setup described in the PhD thesis of Scheer [2]. Highly diluted samples of the hydroxyl phenols in helium were pyrolyzed in an electrically heated 1 mm ID 3.75 cm long short silicon carbide tube and the effluent was expanded into a high vacuum chamber forming a molecular beam in which the molecules are rapidly cooled down to a few degrees to essentially freeze the chemistry. The particular conditions lead to very short residence times on the order of 100 microseconds, which assures that this setup can be used to probe the initial pyrolysis reactions of molecules. Photoionization mass spectrometry and IR matrix spectroscopy were employed to identify the initial products. Using catechol or hydroquinone as starting material, CO was found to be the major initial reaction product along with hydroxycyclopentadiene. This result is in agreement with expectations based on previous studies on phenol decomposition [3]. In the case of catechol, CO formation occurs at higher temperature (1275 K) compared to hydroquinone (1175 K) and in addition, the formation of water and cyclopentadienyl ketene is observed. The

water elimination pathway has been identified theoretically by Altarawneh et al.[4]. No CO_2 formation was detected for either isomer. The initial decomposition product spectrum of resorcinol leads to a different picture because $m/z=66$ (cyclopentadiene) is found as major product at 1275 K leaving CO_2 as only possible second product molecule. At 1375 K, Scheer also observes CO production, but the CO_2 channel remains dominant. No mechanistic explanation of this channel is available. Using a newly designed two stage Frontier micropyrolyzer [5] in which the first stage is used to vaporize the solid reactant and the second to pyrolyze the vapour, Vargas et al. [6] found in resorcinol experiments no evidence for cyclopentadienone (the CO channel) but clearly detected cyclopentadiene and CO_2 . Thus three different setups independently point to some special chemistry in the pyrolysis of resorcinol.

The observed CO formation in catechol and hydroquinone can be understood as reactions analogous to the thermal decomposition of phenol (see Figure 2 left). For catechol ab initio calculations by Altarawneh et al.[4] qualitatively confirm that CO formation is a low energy pathway (see Figure 2 right in which the values in green are updates using CBS-QB3 while all other data are from the original study). A single step water elimination pathway is also identified. Based on an RRKM analysis Altarawneh et al. claim that the water and CO elimination channels are dominating. It should be noted that the phenolic O-H bond in phenol is too strong to allow bond scission to be competitive at the lowest temperatures at which decomposition is observed. For catechol this seems not the case but experimentally there's no evidence for O-H bond scission. This indicates the need to re-investigate the potential energy surface (PES) reported by Altarawneh et al. at a higher level of theory. Another important observation is that ring opening reactions are possible, however, subsequent pathways are unfavorable making these pathways irrelevant for phenol and catechol.

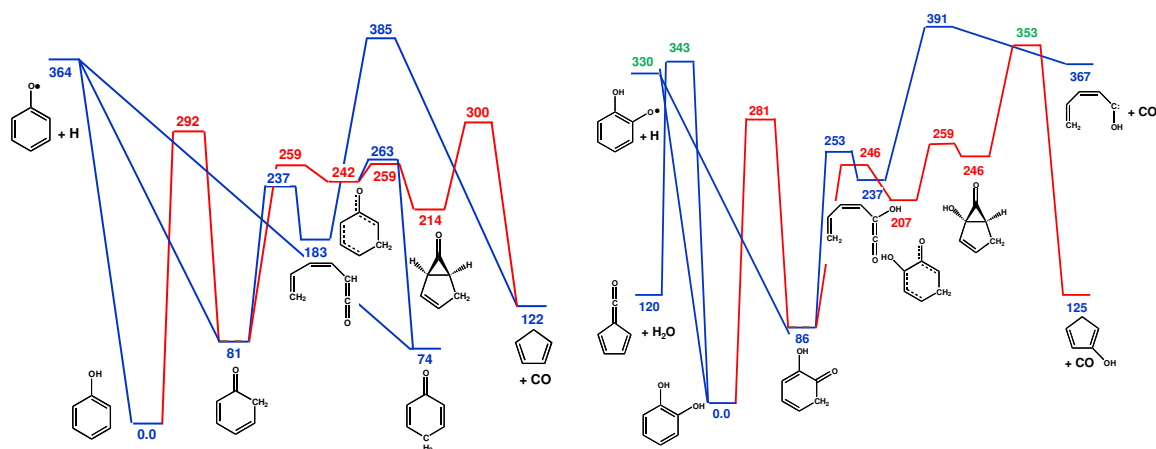


Figure 2: Simplified potential energy surfaces for phenol pyrolysis (left)[3] and catechol pyrolysis (right) adapted from [4]. Energies in kJ/mol at 298 K relative to the initial reactant.

In general, the CO elimination pathway should also be accessible for resorcinol but the experimental results demand that a faster CO_2 pathway must exist for this species. To the best of our knowledge, only the study by Furutani et al. [7] has attempted to explain the initial CO_2 formation observed in resorcinol pyrolysis experiments. This study proposes that CO_2 is formed from the m-benzoquinone diradical, which is formed via two O-H bond scissions. Based on ab initio results on the singlet and triplet surfaces and high-pressure rate constant calculations with transition state theory, the authors finally conclude that the suggested m-benzoquinone diradical mechanism does not provide a fast CO_2 forming route. The pathways would also be inconsistent with the data by Scheer et al. The question, how CO_2 is formed, thus remains open.

Approach and Results

The CBS-QB3 level of theory [8] as implemented in the Gaussian 09 software package [9] has been used to characterize important stationary points on the PES of resorcinol. Except for internal rotations, which are treated separately, the Harmonic Oscillator assumption is applied. Systematic deviations between CBS-QB3 and experimental heats of formation are treated by applying additive bond corrections (BAC). Internal modes resembling rotations are handled as 1-dimensional (1-D) hindered rotors with hindrance potentials calculated at the B3LYP/6-31G(d) level. Reduced moments of inertia are obtained according to the work of East and Radom [10]. Methods from statistical mechanics are used to convert the solutions of the Schroedinger equation for the 1-D internal rotors to partition functions and contributions to the thermodynamic functions.

The search for feasible CO_2 forming pathways in resorcinol was guided by the following assumptions: (1) CO_2 is formed on the $\text{C}_6\text{H}_6\text{O}_2$ PES as an unimolecular reaction, hence no radicals of resorcinol are involved. This provides consistency with the data by Scheer et al. (2) OH ligands do not change positions in benzoic molecules as this would lead to similar chemistries for the three isomers. (3) For bringing the two oxygen atoms together, the ring has to open and possibly close again. Using these guidelines, the pathway shown in Figure 3 is proposed.

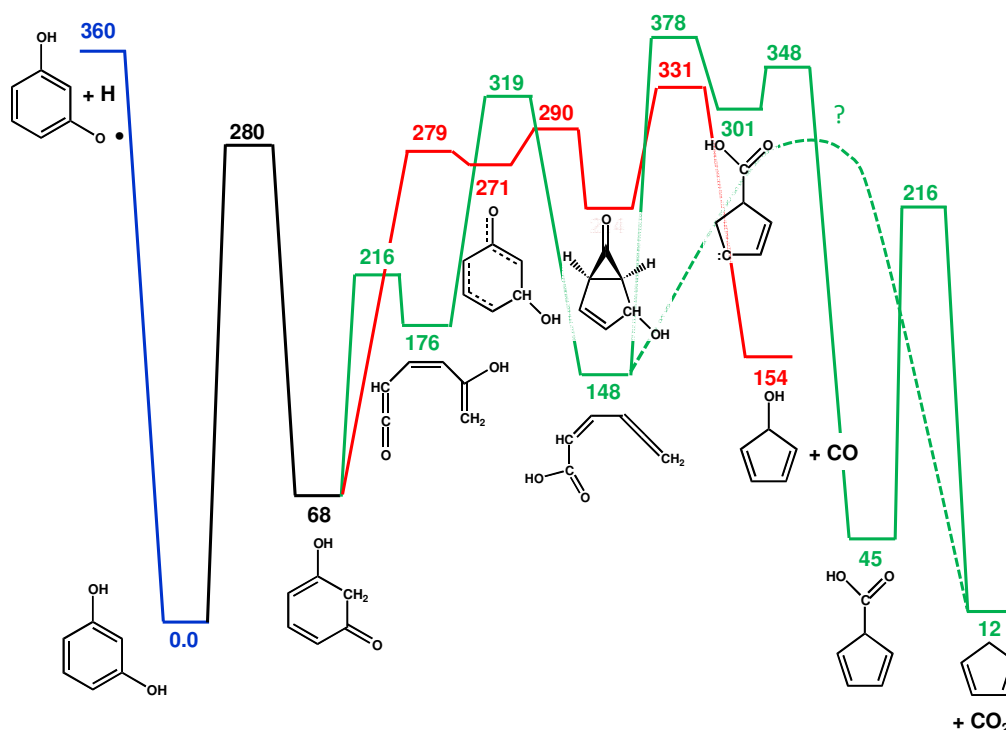


Figure 3: Selected CO and CO_2 formation pathways for resorcinol pyrolysis. Energies are calculated at CBS-QB3 level in kJ/mol at 298 K relative to resorcinol.

The red paths shows a representative low energy route to CO . This pathway is analogous to phenol and catechol. Obviously, several CO formation channels exist as the bicyclic intermediate can ring-open by breaking one of two distinct bonds. Furthermore, two options exist for H migration in resorcinol leading to OH in either ortho or para position to the CH_2 moiety. In Figure 3, only the ortho pathway is included. The key difference to catechol is shown as green pathway: the ring-opening product (2-hydroxybuta-1,3-dienylketene) can further react via a sufficiently low barrier (compared to the highest barrier in the CO elimination pathway) to form 1,2,4-hexatrienoic acid. In this step effectively OH migrates to the carbon that carries the second oxygen atom. Simply judging from the energetics, the

formation of the 1,2,4-hexatrienoic acid should be competitive to the CO elimination channel. If a sufficiently low barrier reaction for the release of CO₂ existed, this mechanism would be consistent with the experimental results discussed above. Work is ongoing to locate a suitable transition state for this final step. So far, two CO₂ elimination channels have been identified (only the lowest energy path is shown), but the barriers of these channels are too high to make them relevant. Current attempts focus on a concerted H migration / CO₂ elimination reaction. An updated PES and a kinetic analysis will be presented in the workshop.

Conclusions

Assuming the elusive low-energy CO₂ elimination step can be located, the proposed pathway has great potential to explain all experimental observations on the initial decomposition chemistry of resorcinol. It suggests that the special structure of the ring-opening step allows for further reactions not possible for the other two hydroxyphenol isomers. From a larger picture point of view, this study demonstrates the high value of reliable experimental results to guide kinetic modelers in the development of complete sets of elementary reactions. For kineticists interested in creating software to automatically construct reaction sets, the pyrolysis of resorcinol presents a reminder that subtle changes in molecular structure might lead to drastic effects and that such software must be able to deal with such subtleties in order to deliver reliable kinetic models.

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