The radical-induced decomposition of 2-methoxyphenol

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The thermolysis of 2-methoxyphenol has been studied between 680 and 790 K, applying cumene as a radical scavenger. Two pathways were observed: a homolytic route involving the cleavage of the methoxyl O–C bond, leading to methane and 1,2-dihydroxybenzene, obeying k_{uni} (s^{-1}) = $10^{15.2 \pm 0.2}$ exp(−239 ± 8 (kJ mol^{-1})/RT), and an induced route starting with abstraction of the phenolic hydrogen by cumyl radicals. After intramolecular hydrogen transfer a cascade of reactions yields phenol, 2-hydroxybenzaldehyde, and 2-hydroxybenzyl alcohol. The latter compound decomposes instantaneously into *o*-quinone methide (*o*-QM) which is reduced to *o*-cresol.

Introduction

Lignin contains numerous methoxyl substituted phenolic structures, stemming from the precursors *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The conversion of lignin into useful (feedstock) chemical compounds has been a challenge for a long time. During pyrolysis and hydrogenolysis complex product mixtures are obtained not only containing various substituted 2-methoxy- and 2,6-dimethoxyphenols, but also *o*-cresol and derivatives, which are believed to originate from the degradation of these methoxyphenols.[1] Besides, a large amount of tarry material is formed, often more than 50%.[1] In order to develop a process that is commercially feasible, it is required that the pyrolysate only contains a limited number of different compounds. Thus, secondary desubstitution reactions may be beneficial to reduce the product spectrum.

(Substituted) 2-methoxyphenols have often been used as model compounds for lignin, *e.g.* in investigations of the effect of solvent, substituents, and processing conditions.[2] However, most of the studies do not detail mechanistic features. Besides homolysis of the weak phenoxyl–methyl bond, a radical-induced pathway appears to be important with 2-hydroxybenzyl alcohol as the reactive intermediate.[2a]

To investigate the contribution of a free radical degradation mechanism in the decomposition of 2-methoxyphenol, the thermolysis of this lignin model compound has been studied in the gas phase between 680 and 790 K, using cumene as the radical scavenger in a well-defined chemical environment.

Experimental

The thermolysis of 2-methoxyphenol was studied with a pyrolysis instrument with off-line GC and GC-MS analysis. Experimental details have been described before.[3] In short: a mixture of 2-methoxyphenol, chlorobenzene (as internal standard), and cumene (molar ratio 6 : 3 : 91) was injected into a nitrogen gas stream and led through a heated plug-flow quartz reactor (effective volume 43.5 ml). The residence times were about 9 s. After 1 h of equilibration, samples were collected at about 195 K and analyzed.

Additional experiments in the liquid phase at elevated temperatures were carried out in pressurized sealed Pyrex tubes. The experimental procedure has been described before.[4] Naphthalene was used as a standard for the quantification of the compounds in the product mixture.

Chemicals

Solid anthracene (Aldrich, >95%) was washed with boiling methanol and the hot solution was decanted. 9,10-Dihydroanthracene (Janssen, 97%) was crystallized twice from boiling methanol before use. All other compounds were obtained from commercial sources in the highest purity and used as received.

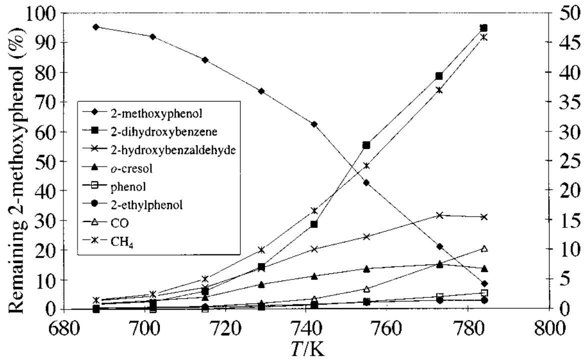


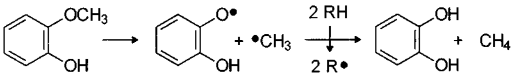
Fig. 1 Conversion and product yields from the thermolysis of 2-methoxyphenol in cumene. Conditions: [cumene] = 2.2 × 10^{-3} M, [2-methoxyphenol] = 1.5 × 10^{-4} M, t = 9.5 s (at 740 K). The methane yield is corrected for the contribution stemming from the cumene pyrolysis (styrene and *tert*-butylbenzene).

Results and discussion

Products and mechanism

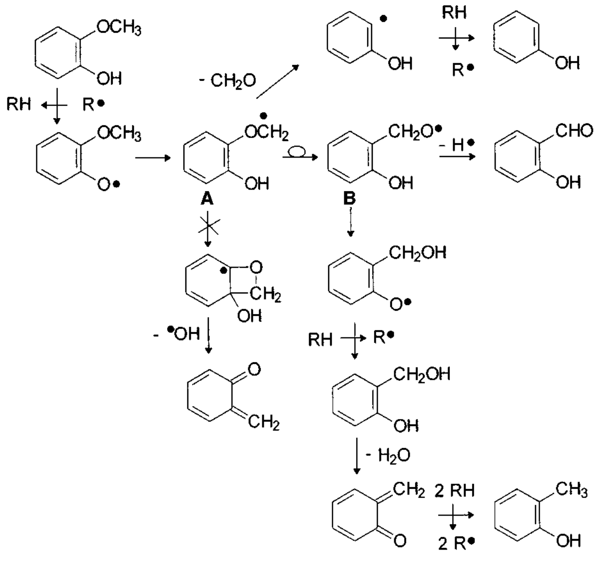
In Fig. 1, the 2-methoxyphenol conversion and product yields between 680 and 790 K are presented. Major products were 1,2-dihydroxybenzene, 2-hydroxybenzaldehyde, *o*-cresol, methane, and carbon monoxide. Small amounts of 2-ethylphenol and phenol were also found (1% and 3% at 784 K, respectively). The mass balance decreased to 89% at 91% conversion of 2-methoxyphenol. Assuming a pseudo-first-order behavior for 2-methoxyphenol, the Arrhenius parameters for the overall decomposition were derived: k_{overall} (s^{-1}) = $10^{12.2}$ exp(−191 (kJ mol^{-1})/RT). Clearly, these parameters are indicative for a mixed homolytic and induced decomposition route.

The homolytic pathway for 2-methoxyphenol starts with the cleavage of the weak phenoxyl–methyl bond. The methyl and the 2-hydroxyphenoxyl radicals abstract a hydrogen atom from cumene to give methane and 1,2-dihydroxybenzene [eqn. (1)].



(1)

The first step in the induced decomposition is the hydrogen abstraction by cumyl radicals, abundantly present in the pyrolysis mixture, from the hydroxy group of 2-methoxyphenol (which is the weakest H–R bond in the molecule). Subsequently, the phenoxyl moiety shuttles a hydrogen from the adjacent methoxyl group to oxygen, leading to intermediate **A** (Scheme 1). Starting from **A**, a rearrangement from $-OCH_2^{\bullet}$ towards $-CH_2O^{\bullet}$ *via* a three-membered ring (1,2 aryl shift) gives intermediate **B**. Elimination of a hydrogen atom from this alkoxyl radical leads to 2-hydroxybenzaldehyde. As a competing reaction, elimination of formaldehyde from **A** provides a 2-hydroxyphenyl radical which, after hydrogen abstraction from the carrier, is converted into phenol. Under these high temperature conditions, formaldehyde eliminates H_2,† resulting in the formation of carbon monoxide.



Scheme 1

The pathway for the formation of *o*-cresol starts from 2-hydroxybenzyl alcohol. This intermediate is not detected since, at the applied temperature, it readily eliminates water to result in *o*-quinone methide (*o*-QM) which in turn is reduced to *o*-cresol (*vide infra*).[6] Retention of configuration for the *o*-cresol formation was verified by performing the thermolysis of 2-methoxy-4-methylphenol. Now the main phenolic product is 2,4-dimethylphenol showing that intramolecular radical addition in **A** (to give a four-membered ring, with subsequent loss of hydroxyl and finally leading to 2,5-dimethylphenol) does not occur.

The transformation of *o*-QM into *o*-cresol consists of a reverse radical disproportionation (RRD) mechanism: the transfer of hydrogen from cumene. For example, at 784 K the RRD rate constant for reaction of *o*-QM with cumene amounts to 87 s^{-1}.‡ This rate constant is apparently high enough to prevent oligomerization of *o*-QM.[6a]

The expulsion of formaldehyde from **A** gains in importance with temperature and hence the ratio (2-hydroxybenzaldehyde + *o*-cresol) : phenol decreased from 42 to 6 between 729 and 784 K. The increase in phenol may also be due to the conversion of 2-hydroxybenzaldehyde into phenol *via* hydrogen abstraction and CO elimination. When related to lignin chemistry (*vide supra*), high reaction temperatures seem to be beneficial to enhance the formation of base chemicals (*e.g.* phenol).

Remarkably, in the thermolysis experiments the CO yield surmounts (3–4 times) the phenol yield (see Fig. 1), while according to Scheme 1 a 1 : 1 ratio would be expected. The thermal decomposition of *o*-QM into benzene and CO[6] is too slow at these temperatures,§ and also CO elimination from the 2-hydroxyphenoxyl radical can be neglected since no CO has been observed in the thermolysis of anisole (to yield phenoxyl radicals) under similar conditions:[9] hydrogen abstraction from cumene is much faster than CO elimination. However, a fraction of the 2-hydroxyphenoxyl radicals can disproportionate with the abundantly present cumyl radicals, yielding *o*-quinone. CO elimination from *o*-quinone is fast and yields cyclopentadienone, which dimerizes into an array of compounds during condensation of the effluent stream.[3] Unimolecular hydrogen elimination from the 2-hydroxyphenoxyl radical to give *o*-quinone can be disregarded as well because of the relatively strong O–H bond in this radical (258 kJ mol^{-1}).¶

Note that the 2-hydroxyphenoxyl radical is not only formed after homolysis of the $O-CH_3$ bond in 2-methoxyphenol, but also after hydrogen abstraction by cumyl radicals from the product 1,2-dihydroxybenzene, similar to the induced decomposition of 2-methoxyphenol. Based on reaction enthalpy assessment, 1,2-dihydroxybenzene may be even more reactive (*vide infra*). The ratio 1,2-dihydroxybenzene : CO_{excess} is around 10, indicating that the hydrogen abstraction by the 2-hydroxyphenoxyl radical from cumene is faster than the elimination of CO. Anyway, the additional CO stems from the homolytic degradation of 2-methoxyphenol.

Kinetics

When 1,2-dihydroxybenzene and the excess CO are considered as the products of the homolysis, the contribution of the unimolecular decomposition to the overall rate of disappearance for 2-methoxyphenol increases with the temperature, from 29% at 702 K to 68% at 784 K. The rate constant for bond homolysis obeys k_{uni} (s^{-1}) = $10^{15.2 \pm 0.2}$ exp(−239 ± 8 (kJ mol^{-1})/RT). After temperature correction (assuming $\Delta C_p \approx 0$: BDE = $E_a + RT_m$ where T_m is the medium temperature and C is the heat capacity), the methoxyl BDE($O-CH_3$) can be derived as 245 kJ mol^{-1}, which is in good agreement with the literature values (*ca.* 243 kJ mol^{-1}).[2b,c] Note that the weakening effect on the BDE($O-CH_3$) by the *ortho*-hydroxy group of 27 kJ mol^{-1} is markedly higher than by an *ortho*-methoxy group (16 kJ mol^{-1}).[3]

The induced decomposition is set in by cumyl radicals, and by using the yield of α-methylstyrene to deduce the cumyl radical concentration,‖ the rate constant for hydrogen abstraction can be estimated:** 4×10^5 M^{-1} s^{-1} at 702 K and 1.5×10^6 M^{-1} s^{-1} at 784 K.

The Arrhenius parameters for the rearrangement **A**→**B** have

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† The Arrhenius parameters for this elimination are: $A = 10^{10.5}$ s^{-1} and E_a = 146 kJ mol^{-1}.[5] The rate constant at 750 K becomes 2 s^{-1}, and a conversion of 99% is reached within 2 s.

‡ For RRD the general Arrhenius parameters are log A = 8.6 (per H) and $E_a = E_0 + 0.82 \times \Delta_r H$ (with E_0 = 37.66 kJ mol^{-1}).[7] With cumene, $\Delta_r H$ becomes 76 kJ mol^{-1},[6a,8] and thus $k_{RRD,cumene}$ (M^{-1} s^{-1}) = $10^{8.6}$ exp(−100 (kJ mol^{-1})/RT).

§ From k (s^{-1}) = $10^{14.8}$ exp(−281 (kJ mol^{-1})/RT)[6a] for the unimolecular decomposition of *o*-QM it follows that the conversion is 0.1% at 784 K.

¶ The O–H bond strength in substituted phenols can be estimated using:[10] ΔBDE(O–H) = 30.63 $\{\Sigma(\sigma_o^+ + \sigma_m^+ + \sigma_p^+)\}$ − 2.68 kJ mol^{-1}; and $\sigma_o^+ = 0.66\ \sigma_p^+$.[11] With BDE(O–H) = 366 kJ mol^{-1} in phenol,[1] and σ_p^+(OH) = −0.92,[12] BDE(O–H) in 1,2-dihydroxybenzene becomes 345 kJ mol^{-1}. Thus, for 2-hydroxyphenoxyl $\Delta_f H$ = −145 kJ mol^{-1} (using $\Delta_f H(H^{\bullet})$ = 218 kJ mol^{-1} and $\Delta_f H$(1,2-dihydroxybenzene) = −272 kJ mol^{-1}).[8] With $\Delta_f H$(*o*-quinone) = −105 kJ mol^{-1},[8] the BDE(O–H) in the 2-hydroxyphenoxyl radical can be estimated as 258 kJ mol^{-1}. With E_a = BDE − RT (when neglecting $\Delta_r C_p$) and $A = 10^{15}$ s^{-1}, the rate for homolysis of the O–H bond in the 2-hydroxyphenoxyl radical becomes 2×10^{-2} s^{-1}, about 10 times slower than the CO elimination.

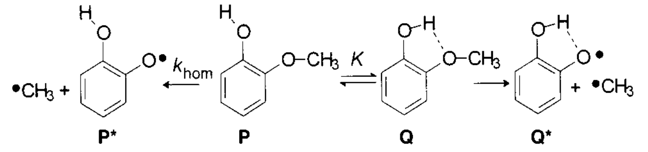
‖ As an assumption: [α-methylstyrene] = $k_{disproportionation} t$[cumyl]^2. With t being the residence time (9.9 s at 702 K, 8.5 s at 784 K), $k_{disproportionation} = 10^9$ M^{-1} s^{-1}, and [α-methylstyrene] = 2×10^{-6} M at 702 K and 5×10^{-5} M at 784 K. As a result [cumyl] = 1.4×10^{-8} M at 702 K and 7.7×10^{-8} at 784 K.

** From $k_{uni} = Q \times k_{ind} \times$ [cumyl], with Q is the fraction of homolytic decomposition divided by the fraction of induced decomposition. $k_{uni} = 1.7 \times 10^{-3}$ s^{-1} at 702 K and 0.175 at 784 K.

been reported[13] as k_{uni} (s^{-1}) = $10^{12.5}$ exp(−88 (kJ mol^{-1})/RT) and thus, from the ratio (2-hydroxybenzaldehyde + *o*-cresol): phenol it can be derived that the rate constant for elimination of formaldehyde from **A** is around 5×10^5 s^{-1} at 784 K, in good agreement with earlier results.[3] The product ratio 2-hydroxybenzaldehyde:*o*-cresol equals 2.3 at 784 K. Most likely, the route to 2-hydroxybenzyl alcohol (and thus *o*-cresol) starts with intramolecular hydrogen abstraction in **B** to give a phenoxyl radical (see Scheme 1). The estimated Arrhenius parameters that have been reported for the hydrogen atom elimination from $PhCH_2O^•$, k (s^{-1}) = $10^{14.1}$ exp(−4.6 (kJ mol^{-1})/RT),[14] predict a rate constant of 6×10^{13} s^{-1} for the formation of 2-hydroxybenzaldehyde. This means that the rate constant for the intramolecular hydrogen abstraction in **B** amounts to 3×10^{13} s^{-1}, which is in accordance with the fact that alkoxyl radicals react rapidly with phenolic hydrogens.

Intramolecular hydrogen bonding

The reagent 2-methoxyphenol and the products 1,2-dihydroxybenzene and 2-hydroxybenzaldehyde exist in two entities: the open structure and the intramolecularly hydrogen bonded form. The latter one is the most stable conformer of 2-methoxyphenol (**Q**, see Scheme 2).



Scheme 2

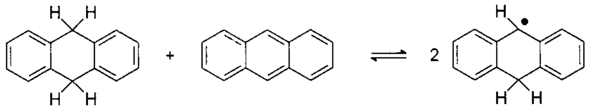
By considering the changes in enthalpy (ΔH(**P**→**Q**) = −16 kJ mol^{-1}) and entropy (ΔS(**P**→**Q**) = 0 kJ mol^{-1} K^{-1}),[15] even at 750 K, 93% exists as **Q**. When the homolytic cleavage takes place only from **Q**, the rate for disappearance of 2-methoxyphenol (**Q** + **P**) is given by $k_{exp} = k_{hom}(K/(K + 1))$. If this is the main pathway (**Q**→**P**→**P***) the experimental activation enthalpy also includes the difference in enthalpy between **P** and **Q**. Our kinetic data show that this is not the case. Thus, the oxygen–carbon bond cleavage occurs without disturbing the hydrogen bond. Interestingly, computational studies have revealed that the enthalpy difference between **P** and **Q** is identical to that between **P*** and **Q*** (16 kJ mol^{-1}) in favour of the hydrogen bonded entity.[15,16]. Hydrogen bonding has no influence on the weakening effect of the hydroxyl group and thus also not on the oxygen–methyl bond strength.

Liquid-phase experiments

Since lignin pyrolysis can only be carried out in the liquid phase, additional experiments with 2-methoxyphenol (0.3 M) have been performed under typical coal liquefaction conditions. Thus, a 1:1 mixture of 9,10-dihydroanthracene (AnH_2, as the hydrogen donor) and anthracene (An), both 2.4 M, was applied as a solvent.

Typically, after a reaction time of 5 h at 625 K, a conversion of 38% was reached. In contrast with the experiments in the gas phase, the mass balance is surprisingly low: the total product yield amounted to only 7%, based on the intake of 2-methoxyphenol: 4% of 1,2-dihydroxybenzene, 2% of *o*-cresol, 1% of phenol, and 0.1% of 2-hydroxybenzaldehyde. The low relative yield of the latter is the result of a highly efficient scavenging of the radicals by the hydrogen donor to give 2-hydroxybenzyl alcohol. This compound is converted quantitatively under these conditions. At high substrate concentrations and high temperatures in the liquid phase we have shown before[4a] that the formation of *o*-QM from this compound does not take place. Instead, a benzylic cation is formed of which the oligomerization *via* electrophilic aromatic substitution is in competition with abstraction of a hydride ion from the solvent and as a consequence the overall mass balance comprising semi-volatile products is reduced.

The induced decomposition is clearly more important in the liquid phase due to the relatively high anthracenyl concentration. From the equilibrium relation for eqn. (2), $K_{eq}(1)$ = 1.3 exp(−132 (kJ mol^{-1})),[17] it follows that [$AnH^•$] = 8×10^{-6} M, predicting a complete conversion of 2-methoxyphenol if the induced decomposition were solely determined by the hydrogen abstraction (with $k_{ind} = 4 \times 10^4$ M^{-1} s^{-1} at 625 K).†† However, in the presence of a high concentration of a hydrogen donor, the hydrogen abstraction is an equilibrium process: hydrogen abstraction from AnH_2 by the phenoxyl radical is in competition with the intramolecular hydrogen abstraction from the methoxyl substituent.



(2)

In retrospect, lignin liquefaction can only be applied if the oligomerization can be prevented by applying highly dilute solutions or appropriate solvents (*e.g.* phenol) which lead to more uniform product distributions.

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†† From the rate constants for induced decomposition in cumene it follows that E_a is *ca.* 37 kJ mol^{-1}, assuming $A = 10^{8.5}$ M^{-1} s^{-1}.[5] From the difference in BDE(C–H) between cumene and AnH_2[18] it can be derived that the E_a for hydrogen abstraction by $AnH^•$ is around 47 kJ mol^{-1} and thus $k_{ind} = 4 \times 10^4$ M^{-1} s^{-1} at 625 K.

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