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Are the Three Hydroxyphenyl Radical Isomers Created Equal? – The Role of the Phenoxy Radical –

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We have investigated the thermal decomposition of the three hydroxyphenyl radicals (•C₆H₅OH) in a heated microtubular reactor. Intermediates and products were identified isomer-selectively applying photoion mass-selected threshold photoelectron spectroscopy with vacuum ultraviolet synchrotron radiation. Similarly to the phenoxy radical (•C₆H₅–O•), hydroxyphenyl decomposition yields cyclopentadienyl (•C₅H₅) radicals in a decarbonylation reaction at elevated temperatures. This finding suggests that all hydroxyphenyl isomers first rearrange to form phenoxy species, which subsequently decarbonylate, a mechanism which we also investigate computationally. Meta- and para- radicals were selectively produced and spectrascopically detectable, whereas the ortho isomer could not be traced due to its fast rearrangement and rapid decomposition in the reactor. A smaller barrier to isomerization to phenoxy was found to be the reason for this observation. Since hydroxyphenyl species may be present under typical sooting conditions in flames, the resonantly stabilized cyclopentadienyl radical adds to the hydrocarbon pool and can contribute to the formation of polycyclic aromatic hydrocarbons, which are precursors in soot formation.

Introduction

Oxidated radicals, such as phenoxy (•C₆H₅–O•) play a large role in biological and environmental processes as transient species. 1 Substituted or metal-complexed phenoxy radicals are commonly encountered in larger biomolecules such as microperoxidase and galactooxidase 2 – important compounds in biocatalysis. 3 In addition, phenoxy moieties are common linkages in lignin macromolecules, which can be cracked by fast-pyrolysis techniques to yield more valuable fine chemicals and fuels. 4,9 Recently, we have investigated the thermal decomposition of diphenylether (DPE), a lignin model compound, and found that phenyl (•C₆H₅) and phenoxy radicals are the major decomposition products at low temperatures. 10 It is well known that resonantly-stabilized phenoxy radicals are common intermediates in combustion processes. 11 Besides the reaction of OH radicals with benzene to form phenyl radicals (1) or phenol (2), it was found that the formation of phenoxy radicals (3) contributes significantly to the fuel consumption pathways in benzene/oxygen/argon flames. 12-14

C₆H₆ + OH → C₆H₅ + H₂O (1)
C₆H₆ + OH → C₆H₅OH + H (2)

C₆H₅ + O(3P) → C₆H₅O + H (3)

The oxygenation of phenyl radicals with molecular oxygen (4) through an elusive phenylperoxy intermediate can also contribute to the formation of phenoxy radicals: 15-18

C₆H₅ + O₂ → C₆H₅–OO → C₆H₅ + O (3P) (4)

Several phenoxy consumption reactions are also known to play a major role, such as the unimolecular decomposition to form cyclopentadienyl and carbon monoxide (5) or hydrogen abstraction to yield phenol (6). 11

C₆H₅O → C₆H₅ + CO (5)
C₆H₅O + H → C₆H₅OH (6)

In particular, the unimolecular decomposition (5) of phenoxy radicals is well understood. Cyclopentadienyl radicals can subsequently lose acetylene to yield propargyl radicals following reaction (7).

C₆H₅ → C₆H₃ + C₂H₂ (7)

Both propargyl and cyclopentadienyl are resonantly stabilized radicals, which are – on account of their long lifetime and resistance to oxidation – known to be efficient precursors of benzene C₆H₆ 19-22 and naphthalene C₁₀H₈. 23-25 These reactions are believed to be key cyclization and ring growing steps that initiate the formation of larger polycyclic aromatic hydrocarbons (PAHs) and soot. 26, 27

The oxidation of benzene by OH addition to yield phenol (2) is a key step in the oxidation chemistry of aromatic fuels. 14

Hydrogen atom abstraction from the hydroxyl group can lead to phenoxy radicals, which are in turn unreactive towards oxidation, but decompose unimolecularly (5). However, it is also conceivable that H-abstraction from the ring or the fragmentation of larger aromatics leads to the formation of...
1.3–1.5 bar, in a resistively heated SiC microtubular reactor detected by a Jordan-TOF MCP detector. Hydroxyphenyl radicals were produced from 2-, 3- and 4-iodophenol hydroxyphenyl radicals has recently been investigated by time.

Experimental and Theoretical Methods

Experiments were carried out at the VUV beamline of the Swiss Light Source in Villigen, Switzerland. Vacuum ultraviolet light is generated by a bending magnet and transferred to the experimental station by three optical elements. The light is intersected with a molecular beam in the ionization region of the iPEPICO apparatus. A 120 V/cm field extracts the electrons, which are velocity map imaged (VMI) onto a Roentdek DLD40 delay line anode detector. The detection of an electron tags the time zero for the time-of-flight ion signal. Thus the temperature of the sample container was set to minimize the amount of HI and other products from bimolecular chemistry, while being still high enough to obtain an acceptable signal-to-noise ratio in the unimolecular channels. The temperature of the reactor was measured by a type-C thermocouple at the surface of the SiC tube. According to the detailed study by Guan et al., the centerline temperature in the reactor can be up to 25 % less than the outside surface temperature of the reactor wall with argon bath gas. Based on the computational fluid dynamics simulations of Guan et al., we estimate the pressure at the entrance of the reactor after the flux-reducing 100 μm pinhole to be several tens of mbar. When the pyrolysed sample leaves the reactor ca. 10–100 μs later, the pressure drops several orders of magnitude to 10–4 mbar. The molecular beam is skimmed by a 1 mm I.D. Beam Dynamics skimmer and intersected with the VUV light in the spectrometer chamber. We measured temperature dependent mass spectra at different photon energies to determine the reaction pathways. Photoionization (PI) spectra were obtained by scanning the photon energy in 10–20 meV steps and averaging for 120 to 300 s per point in order to identify different isomers. In case of PI spectra all kinetic energy electrons were selected in the coincidence scheme, whereas only near threshold energy electrons (Ekin < 5 meV ) were selected in typical ms-TPES scans. The energetic (hot) electron contamination in the VMI images was subtracted by a procedure as suggested by Sztaray et al.

Computations were performed utilizing the Gaussian09 suite of programs. For the Franck–Condon simulations, we used ezSpectrum.OSX with geometries and force constant matrices obtained at the B3LYP/6-311++G(d,p) level of theory. Ionization energies were calculated applying the CBS-QB3 composite method, including zero-point corrections. For the potential energy surface of hydroxyphenyl radicals, the G3X-K theory was applied.

Mass Spectrometric Analysis

In order to determine the decomposition pathways, we have measured mass spectra as a function of the reactor temperature at a photon energy of 9 eV as shown in Figure1 (a) for 2-iodophenol.
The decomposition of the 2-iodophenol precursor to 2-hydroxyphenyl starts at around 600 °C. Complete decomposition is observed at temperatures above 700 °C. The appearance of $m/z = 65$ can be attributed to cyclopentadienyl ($c$-$C_5H_5$) and the trace amounts of $m/z = 93$ and 94, to 2-hydroxyphenyl ($C_6H_4$OH) or phenoxy radicals, and phenol ($C_6H_5$OH), respectively. The $m/z = 220$ signal is attributed to the iodophenol radical precursor. It should be noted that the iodine loss at the β-carbon site of the precursor indeed results in 2-hydroxyphenyl, but its fast disappearance indicates subsequent rapid unimolecular decomposition to cyclopentadienyl. Above 700 °C, propargyl radical ($m/z = 39$) and acetylene (see supporting information Figure S1) signals appear, corresponding to fragments of the $C_6H_5$ radical. The overall reaction sequence is depicted in Scheme 1.

![Scheme 1](image)

Scheme 1 Decomposition pathway of $n$-iodophenol ($n = 2–4$). The hydroxyphenyl radicals rearrange to phenoxy and undergo decarbonylation to yield cyclopentadienyl radicals, and finally form propargyl radicals by acetylene loss.

The PI-MS of meta-iodophenol, displayed in Figure 1(b) as a function of the reactor temperature, shows some differences when compared to the ortho-iodophenol spectra. A greater $m/z = 93$ signal intensity points to an increased stability of 3-hydroxyphenyl towards both isomerization and decomposition (vide infra) compared to 2-hydroxyphenyl radicals. Here again, phenol at $m/z = 94$ is produced via bimolecular chemistry, when the highly reactive 3-hydroxyphenyl abstracts a hydrogen atom, e.g., from the non-pyrolyzed precursor. If the temperature is steadily increased, we observe the degradation of the $C_6H_5$O ($m/z = 93$) signal, while $c$-$C_5H_5$ ($m/z = 65$) is formed after CO loss. Indeed, both 2- and 3- and 4-hydroxyphenyl (see supporting information Figure S2) isomers follow the same decomposition pattern forming $C_6H_5$ and $C_5H_5$ species. This decomposition chemistry is different from the unsubstituted phenyl radical, which forms benzene after a hydrogen loss, which in turn yields acetylene and diacetylene; hydroxyphenyl radicals do not show any convincing evidence for decomposition pathways leading to hydroxybenzene ($m/z = 92$) or hydroxydiacetylene ($m/z = 66$).

The decomposition products and the more abundant intermediates can be assigned isomer specifically by their mass-selected threshold photoelectron spectra and, in some favourable cases, even by their photoionization spectra. Figure 2 shows ms-TPE spectra of $m/z = 65$ and 39 as measured from decomposing 2-hydroxyphenyl radicals generated upon pyrolysis of 2-iodophenol. The feature at 8.43 eV of the black trace ($m/z = 65$) is in good agreement with the adiabatic ionization energy of cyclopentadienyl radicals, which is assigned to the $\tilde{X}^2E_1 \rightarrow \tilde{X}^1A_2$ transition. At 8.62 eV, a second ion state can be populated, which was assigned to the $\tilde{X}^2E_1 \rightarrow \tilde{1}^1E_2$ transition by Wörner and Merkt. Trace amounts of $l$-$C_5H_5$ also contribute to the threshold ion signal between 8.0 and 8.2 eV, and their involvement in the reaction pathways might also be noticeable in light of recent findings.

A mechanism for the formation of $l$-$C_5H_5$ and the PIE curve showing some evidence is displayed in the ESI (Figures S3 and S4). The propargyl radical ($m/z = 39$), is responsible for the feature arising at 8.70 eV ($\tilde{X}^4B_2 \rightarrow \tilde{X}^1A_1$). The ms-TPE spectra of propargyl and cyclopentadienyl from decomposing 3- and 4-hydroxyphenyl radicals are nearly identical to those shown in Figure 2.

![Figure 2](image)

Figure 2 ms-TPE spectra of 2-hydroxyphenyl decomposition products. The spectra are nearly identical for the isotopes $n = 2–4$. The spectra can be assigned to propargyl ($m/z = 39$, red open circles), cyclopentadienyl ($m/z = 65$, black open squares).
The above results indicate that, independently of the specific isomer formed from iodophenol, the final products of hydroxyphenyl radical decomposition are \( c-C_6H_5 \) and \( cH_3 \) radicals. Since the first reaction on the way to \( c-C_6H_6 \) and \( cH_3 \) is a CO loss, it is likely that the 2-, 3- and 4- hydroxyphenyl radicals first isomerize to the phenoxy radical and subsequently decompose according to Scheme 1.

**Spectroscopic evidence for hydroxyphenyl radicals**

The question now arises if one can disentangle the intermediate species in mass channel \( m/z = 93 \), which could correspond to one specific \( C_5H_5O \) isomer or a mixture of them. Therefore, we attempted to measure ms-TPE and PI spectra of \( m/z = 93 \) of all the three hydroxyphenyl isomers. 2-Hydroxyphenyl derived from 2-iodophenol could not be detected in measurable amounts at any reactor temperature by PI spectra or ms-TPES, indicating a rapid decomposition directly or after a very fast isomerization to an unstable compound. Figure 3 shows photoionization efficiency (PIE) curves, also called photoionization (PI) spectra, of \( m/z = 93 \) after pyrolysis of 4- (blue open circle) and 3-iodophenol (red open rectangles) at around 650 °C reactor temperature. The black curve in Figure 3 was obtained from an earlier experiment where we investigated the decomposition of diphenylether (DPE), which, after a C–O cleavage reaction, yields phenyl and phenoxy radicals as intermediates (Scheme 2). 10

![Scheme 2](image_url)

The reference PI spectrum for phenoxy (black triangles) exhibits a steeper slope between 8.55 and 8.8 eV than the curves for \( m/z = 93 \) obtained from 3-hydroxyphenol (red squares) and 4-hydroxyphenol (blue circles). The \( m/z = 93 \) isomers derived from the iodophenol precursors produced a higher ion signal than phenoxy alone at photon energies as low as 8.2 eV, suggesting that there are \( m/z = 93 \) species present with lower ionization energies than the phenoxy isomer. However, PI spectra are subject to temperature effects because of unresolved hot- and sequence bands that can shift the ionization onset to lower photon energies. On the other hand, ms-TPE spectroscopy can be used to address this issue, since vibronic transitions from the neutral into the ion’s manifold can often be resolved. Ms-TPE spectra of \( m/z = 93 \) obtained from 3-iodophenol pyrolysis at 650 °C are depicted in Figure 4 along with the experimental spectrum of the phenoxy radical, showing marked differences between the two spectra.

Indeed, these observations are supported by the calculated and experimental ionization energies of phenoxy and hydroxyphenyl radicals in Table 1. The relatively high ion yield at energies between 8.2 and 8.6 eV (Figure 3) cannot be due to phenoxy alone but indicates the presence of sizable amounts of hydroxyphenyl isomers. On the other hand, the slow and structureless increase of the TPE signal (Figure 4 b) indicates small Franck-Condon factors close to the adiabatic ionization energy of hydroxyphenyl radicals. Quantum chemical calculations reveal that there is significant distortion of the C-C-C angle of the hydroxyphenyl radicals upon ionization, which results in poor Franck–Condon factors at the ionization threshold. Franck–Condon simulations of the TPE spectra of phenoxy (Figure 4 (a)) and 3-hydroxyphenyl (Figure 4 (b)) radicals are in accord with the experimental spectra. The spectrum of the phenoxy radical shows a well resolved peak at 8.56 eV, which can be assigned to the adiabatic ionization energy in agreement with Dewar and David. 54 Due to the large step size of 50 meV the second transition at 8.62 eV is not resolved. Nonetheless, both the experimental and simulated spectra are in reasonable agreement and confirm the presence of phenoxy radicals upon pyrolysis of DPE.

The TPE spectrum in Figure 4 (b) is clearly different from the experiments with DPE as precursor. No pronounced feature at 8.56 eV is present, which should show up despite the rather low resolution of 20 meV. In addition, a FC simulation (sticks and Gaussian convolution fwhm = 20 meV) is also depicted, showing a large density of transitions from the neutral into the ion’s ground state. However it does not reproduce the peak at around 8.75 eV, which could be caused by transitions into the triplet state of the 3-hydroxyphenyl ion, calculated to be at 8.71 eV by CBS-QB3. In summary the TPE and PI spectra of \( m/z = 93 \), as synthesized from 3- and 4-iodophenol (see ESI), are clearly different from that of the phenoxy radical. This substantiates the assumption that the hydroxyphenyl radicals...
are formed as intermediate radicals on the way to cyclopentadienyl and propargyl.

![ms-TPES spectra and FC simulations of (a) phenoxy derived from diphenylether, and (b) 3-hydroxyphenyl derived from 3-iodophenol. A vibrational temperature of 500 K was assumed in the FC simulations.](image)

**Figure 4** ms-TPES spectra and FC simulations of (a) phenoxy derived from diphenylether, and (b) 3-hydroxyphenyl derived from 3-iodophenol. A vibrational temperature of 500 K was assumed in the FC simulations.

<table>
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<tr>
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<th>B3LYP/6-311+G(3p,d)</th>
<th>CBS-QB3</th>
<th>exp. eV</th>
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<tr>
<td>phenoxy</td>
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<td>8.71</td>
<td>8.66</td>
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<tr>
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<tr>
<td>4-hydroxyphenyl</td>
<td>8.30</td>
<td>8.27</td>
<td>8.1 ± 0.2</td>
</tr>
</tbody>
</table>

**Table 1** Calculated and experimental ionization energies of four different C$_7$H$_7$O isomers. The ionization potential of 3- and 4-hydroxyphenyl radicals are comparable but different from the one of phenoxy.

Computed Decomposition Mechanism

Of particular interest is the finding that we can generate 3- and 4-hydroxyphenyl radicals from their corresponding iodophenols, however their decomposition products are ultimately the same as those of the phenoxy radical: the formation of cyclopentadienyl + CO and, at higher reactor temperatures, propargyl + acetylene. This points to phenoxy radical as a shared intermediate on the way to the formation of cyclopentadienyl + CO and, at higher reactor temperatures, propargyl + acetylene.

The potential energy surface shown in Figure 5 holds the key to understanding why we found it impossible to measure the PI/ms-TPES spectrum of the 2-hydroxyphenyl radical. It is obvious that both 3- and 4-hydroxyphenyl possess deeper minima compared to the ortho isomer (≈ 60 vs. 40 kcal/mol), due to steric effects when accessing the three- and four-membered transition states, as mentioned earlier. If we now neglect the influence of the hydroxyl group on the C–I bond dissociation energy of the iodophenol precursors, the bond dissociation energy should be comparable with that in phenyl iodide (67.4 kcal/mol). In case of 2-hydroxyphenyl, the entrance barrier to form the radical (C–I bond cleavage) is larger than the activation energy to phenoxy isomer, and at the corresponding temperature, 2-hydroxyphenyl can promptly rearrange to phenoxy and subsequently dissociate.
This underlines the role of the apparently fast rethermalization occurring in the reactor. The C–I loss to form the 2-hydroxyphenyl radical takes place in the sweet spot of the reactor\textsuperscript{27} (relatively long residence times of several 100 μs) and the 2-hydroxyphenyl thus also completes the subsequent reaction steps, namely rearrangement to phenoxy and decomposition to cyclopentadienyl. We have found similarly fast re-thermalization in the decomposition of the flame retardant molecule dimethyl methyl phosphonate (DMMP)\textsuperscript{57}.

In contrast to the 2-hydroxyphenyl radical, nascent 3- and 4-hydroxyphenyl radicals are less prone to isomerization/decomposition, and can survive at the lower range of reactor temperatures required to achieve C–I bond homolysis in the parent compounds. Moreover, in all three cases the barriers required for hydroxyphenyl rearrangement to phenoxy (TS1, TS2, TS3) lie at energies above those required for further isomerization and decomposition to cyclopentadienyl + CO (TS4, TS5, TS6). We therefore expect thermal decomposition to proceed without the intermediacy of collisionally stabilized phenoxy (i.e., in a well-skipping process).

**Conclusions**

We have investigated the decomposition of the three hydroxy-substituted phenyl radical isomers, synthesized from iodophenol precursors in a heated microtubular reactor. Using the iPEPICO technique in combination with VUV synchrotron radiation, we were able to unambiguously identify 3- and 4-hydroxyphenyl radicals by mass-selected threshold photoelectron spectra, in contrast with the more ambiguous interpretation of slight differences in the photoionization spectra. The ms-TPE spectra of 3- and 4-hydroxyphenyl radicals do not display vibrationally-resolved peaks, a fact that is attributed to the large change in geometry upon ionization. However, these spectra are significantly different from that of the phenoxy radical, the global minimum on the C\textsubscript{6}H\textsubscript{5}O potential energy surface. The three hydroxyphenyl radicals can isomerize by hydrogen-shifts towards the resonantly stabilized phenoxy radical, and decompose immediately at elevated temperatures. We have constructed a potential energy surface, which connects all hydroxyphenyl isomers over three and four-membered transition states to the phenoxy radical. Direct hydrogen abstraction reactions to yield hydroxy-substituted benzenes all lie higher in energy. The phenoxy radical can decompose to form cyclopentadienyl radicals and carbon monoxide at medium reactor temperatures. Due to the fact that the 2-hydroxyphenyl is less stable towards rearrangement to phenoxy than the 3- and 4-isomers, it does not survive when formed from its 2-iodophenol precursor.

These rearrangement reactions are essential for the understanding of combustion processes, since there is another route to form phenoxy radicals apart from reactions 3 and 4, namely by rearrangement of hydroxyphenyl radicals. This formation can subsequently increase the amount of cyclopentadienyl, which dimerizes according to reaction 8 yielding naphthalene:

\begin{equation}
\text{c-C}_7\text{H}_5 + \text{c-C}_7\text{H}_5 \rightarrow \text{C}_{10}\text{H}_{10} \rightarrow \text{C}_{10}\text{H}_8 + \text{H}_2 \quad (8)
\end{equation}

Since hydroxyphenyl moieties are also present in lignin macromolecules mimicking the β-O4 bond, it is also conceivable that their decomposition to cyclopentadienyl and propargyl can also significantly contribute to the coking process. As a consequence, soot formation can be promoted, which may lead to blocked catalyst pores and covered active sites, effectively deactivating the catalyst in, e.g., catalytic fast pyrolysis of lignin via decarbonylation\textsuperscript{58,59}.

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Notes and references

The authors declare no competing financial interest.

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