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Formation and stabilization of persistent free radicals

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Abstract

We demonstrate that stable and relatively unreactive "environmentally persistent free radicals (PFRs)" can be readily formed in the post-flame and cool-zone regions of combustion systems and other thermal processes. These resonance-stabilized radicals, including semiquinones, phenoxyls, and cyclopentadienyls, can be formed by the thermal decomposition of molecular precursors including catechols, hydroquinones and phenols. Association with the surfaces of fine particles imparts additional stabilization to these radicals such that they can persist almost indefinitely in the environment. A mechanism of chemisorption and electron transfer from the molecular adsorbate to a redox-active transition metal or other receptor is shown through experiment, and supported by molecular orbital calculations, to result in PFR formation. Both oxygen-centered and carbon-centered PFRs are possible that can significantly affect their environmental and biological reactivity.

Keywords

Semiquinone radical; Phenoxyl radical; Cyclopentadienyl radical; Particulate matter

1. Introduction

With publication of epidemiological data in 1990 that linked exposure to airborne fine particles (PM2.5) and cardiopulmonary diseases, the impact of exposure to PM2.5 on human health has become a major environmental issue [1,2]. Rather nebulous physical factors such as particle size and surface area have been identified as significant factors in health risk [3]. Acidity, sulfates, peroxides, and reactive metals have been proposed as the causative agents [3]. The variation in organic composition, presence of black carbon (soot), and the role of biological material have also been the subject of study as causative agents [4]. These factors are largely concerned with the presence of stable atomic, molecular, or macromolecular species in fine particles. However, we and other researchers have recently generated evidence that airborne fine particles and combustion- generated particles contain environmentally persistent free radicals (PFRs) that have the potential to induce oxidative stress and a variety of illnesses in exposed populations [5–8].

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It is well documented that free radicals with unpaired electrons can exist under special circumstances and can be detected by various analytical techniques including electron paramagnetic resonance spectroscopy (EPR). Small radicals, such as hydroxyl are very stable (viz. do not decompose), but are highly reactive (viz. react with other radicals or molecules). Small organic radicals, such as phenyl, vinyl, or methyl, are somewhat less reactive but are also less stable [9]. Recently, it has been realized that resonance stabilized radicals, such as cyclopentadienyl, propargyl, and phenoxyl are not highly reactive with molecular species, including oxygen, and can undergo radical– radical recombination reactions to form polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F), PAH and possibly soot at moderately high temperatures in the post-flame and cool-zone region of combustion and thermal processes [10,11]. Less well known are semiquinone radicals that are resonance stabilized, already partially oxidized, and are sufficiently non-reactive that they can exist for seconds in air or oxygenated solutions (cf. Fig. 1) [12].

Semiquinone radicals exist in cigarette smoke, and some of the health impacts of smoking have been attributed to oxidative stress induced by redox-cycles that produce biologically damaging reactive oxygen species (ROS) such as peroxide, superoxide, and hydroxyl radical. The observation of semiquinone radicals in cigarette smoke suggests that these radicals may also be present in the effluent from a variety of combustion sources, including biomass fuels, fossil fuels, and hazardous materials where chlorine may further stabilize these radicals. Particularly intriguing is evidence that the association of radicals with the surface of some particulate matter can further stabilize the radicals to the point that they are persistent in the atmospheric environment and may be transported over considerable atmospheric distances [13]. We have previously obtained EPR spectra of samples of various combustion-generated fly-ashes (primarily inorganic silica/alumina), soots (primarily black carbon), and airborne fine particles (PM2.5) [5,14]. The EPR spectra were broad and featureless indicating the presence of multiple radicals or strong matrix interactions. However, these analyses indicate that each sample contains free radicals in concentrations of 10^{16}–10^{17} spins/g which is comparable to that found in cigarette smoke [14].

This manuscript addresses the potential for formation of semiquinone-type PFRs (of the general structure: ■O-phenyl-OH) from likely hydrocarbon and chlorinated hydrocarbons molecular precursors: hydroquinone (*p*-dihydroxybenzene), catechol (*o*-dihydroxybenzene), phenol, 2-chlorophenol, chlorobenzene, and 1,2-dichlorobenzene. It expands on previous studies in our laboratory through reporting of matrix isolation spectra of cyclopentadienyl radical and other potential PFRs; density functional theory (DFT) calculations of stabilities, reactivities, and valence electron densities of potential PFRs; and providing additional data and detailed interpretation of EPR spectra of PFRs on surrogate CuO/silica particles.

2. Experimental description

The experiments were designed to provide a laboratory simulation of the post-flame, thermal and down-stream, cool-zones of a generic combustion system. The thermal zone may form radicals and other pollutants via gas-phase reactions (600–1200 °C). In the cool-zone, lower temperatures (100–600 °C) result in condensation of chemicals on the surfaces of particles that can catalyze additional pollutant and radical formation.

Low Temperature Matrix Isolation EPR (LTMI-EPR) was used for detection, and characterization of trace quantities of radicals produced at high temperature in gas-phase reactions. Experiments were carried out by loading hydroquinone (HQ), catechol (CT), or phenol (Ph) (>99.5% pure) into a Pyrex vaporizer maintained at 50 °C and a total pressure of carrier gas (CO_2 or N_2) in the range of ~0.1–0.3 torr. The vaporized sample was passed through a tubular-flow quartz reactor (i.d. = 12 mm, length = 40 mm) at a feed rate of ~10^{-3}–10^{-2} mmol/min. The gas-phase residence time was ~10 ms and the reaction temperature was varied between 400 and 800 °C. Radical accumulation times ranged from 10 to 15 min. Pyrolysis products were condensed onto the cold finger of the Dewar placed in the EPR cavity and cooled by liquid nitrogen. Carbon dioxide (or other gases that can be used to generate an appropriate matrix) was introduced as a post-pyrolysis, side stream or as a main carrier gas into pyrolysis zone.

Ab initio calculations were performed using the Gaussian 03 suite of programs installed on computational facilities at the LSU. We compared B3LYP/6-31G(d,p), BHandHLYP/6-31G(d,p), and QCISD(T)/6-31G(d,p)//B3LYP/6-31G(d,p) for selected reactions (see Table 1) and found that all three methods gave the same relative ordering of activation energies and then, for computational efficiency, chose to use both the B3LYP and BH and HLYP for all our calculations. The energies were unscaled and zero-point corrected. Transition states were located by performing relaxed potential energy surface scans followed by implementation of a Synchronous Transit-guided Quasi-Newton (STQN) method.

Surface stabilized radicals were synthesized *in vacuo* by dosing surrogate particles of 5%CuO on silica with vapors of phenol, 2-chlorophenol, chlorobenzene, and 1,2-dichlorobenzene, catechol and hydroquinone at < 10 torr over a temperature range of 150–350 °C. The CuO/silica particles represent a surrogate for combustion-generated flyash that contain catalytically active transition metals. Other metals, such as iron and nickel, may also be catalytically active. After chemisorption, the samples were evacuated to 1×10^{-2} torr and the EPR spectrum were obtained using a Bruker EMX Spectrometer.

3. Results and discussion

At the outset of this work, it was not clear which molecular precursors could form PFRs and just how stable the PFRs would be under various combustion conditions. For example, a PFR might form readily from thermal degradation of a precursor; but it could be readily oxidized by reaction with molecular oxygen (which is the principal fate of most organic radicals) or the radical might simply decompose. However, association of the radical with a particle in the cool-zone of a combustor might stabilize the radical and prevent oxidation. By being associated – with and stabilized on a fine particle, an additional route of human exposure and health impacts is created.

We examined the propensity for formation of PFRs via purely gas-phase, thermal reactions using matrix isolation techniques to trap the free radicals for analyses by EPR. We assessed the intrinsic gas-phase stability of these radicals via DFT calculation techniques. We determined whether they can be formed and stabilized by particles by dosing various radical precursors on fly-ash surrogates under cool-zone conditions.

3.1. Matrix isolation studies of free radicals

Although it is likely that there are many unrecognized sources and precursors of PFRs in the environment, diesel exhaust particulate, wood smoke, and cigarette smoke are documented sources of hydroquinones and catechols [15,16]. These classes of molecules can decompose via hydrogen atom loss to form semiquinone radicals (cf. Fig. 1). However, hydroquinones and catechols can decompose at elevated temperatures in combustion systems to form other resonance stabilized radicals such as phenoxyl, cyclopentadienyl, and hydroxycyclopentadienyl as also depicted in Fig. 1.

We pyrolyzed hydroquinone, catechol, and phenol over the temperature range of 300– 750 °C and cryogenically trapped the products at 77 K in EPR tubes. EPR spectra were broad and featureless unless carbon dioxide was used as an isolation matrix. As the pyrolysis temperature was raised, the EPR spectra gradually simplified and resolved (cf. Fig. 2). Annealing of the matrix by raising the temperature of the cold finger and re-cooling to 77 K resulted in apparent annihilation of more reactive radicals and sharpening of the spectra. Based on comparison to the literature and calculated EPR spectra, the annealed EPR spectrum resulting from pyrolysis at 750 °C was identified as that of cyclopentadienyl radical. Virtually identical spectra were obtained from pyrolysis of hydroquinone and phenol, further supporting the identification of the radical observed at 750 °C as cyclopentadienyl radical formed by the left-hand pathway in Fig. 1.

Although only the resonance-stabilized, cyclopentadienyl radical was clearly identifiable at elevated temperatures, the broader spectrum observed at low field strengths may be the anticipated semiquinone and/or phenoxyl radical. Potential superposition of the spectra of these, and possibly other, radicals makes conclusive identification difficult and additional work is necessary to identify conditions where a single radical is formed that would allow conclusive EPR identification.

The direct observation of cyclopentadienyl radical from pyrolysis of hydroquinone, catechol, and phenol suggests it may also be a PFR in combustion and thermal systems. While semiquinone and phenoxyl radical would be expected to be resistant to oxidation, it is likely that they would thermally decompose above 700 °C. In contrast, cyclopentadienyl is more resistant to thermal decomposition and can survive under the pyrolytic conditions of these experiments. Under oxidative conditions, cyclopentadienyl radical may be more susceptible to oxidation than semiquinone and phenoxyl radicals and, therefore, less persistent.

It is important to note that hydroquinone/catechols can be considered as surrogates for other, more complex oxy-PAH emitted from combustion systems that may also lead to formation of semiquinone- type PFRs.

3.2. Calculation of PFR stabilities and reactivities

Organic radicals may be consumed by unimolecular decomposition at elevated temperatures or by chemical reaction, primarily with high-concentration molecular species, at all temperatures. In the case of semiquinone radicals of hydroquinone and catechol as well as phenoxyl radical, the principal route of decomposition is expected to be expulsion of carbon

monoxide [17] In air, the primary reaction pathway of radicals is with molecular oxygen to form the corresponding peroxide (cf. Fig. 3) [18].

The activation energies and reaction energies (latter not shown) for the: (a) formation of these radicals from the unimolecular decomposition of the molecular precursors, (b) decomposition by elimination of carbon monoxide, and c) addition of oxygen are depicted in Fig. 3 as calculated using a BHandHLYP/6-31G(d,p) basis set using the Gaussian 03 suite of programs.

The numbers given over each arrow are the activation energies of these processes in kcal/mol. The calculation indicates that the *ortho*-semiquinone radical is slightly easier to form and slightly more resistant to decomposition or oxidation than *para*-semiquinone radical. The results also suggest that phenoxyl is slightly more difficult to form than semiquinone radicals and is slightly less resistant to decomposition than semiquinone radicals. The calculations indicate that the reaction of phenoxyl radical with oxygen has an activation energy comparable to that of semiquinone radicals.

Free energy calculations indicate that the reaction of molecular oxygen with phenoxyl or semiquinone radicals is highly endothermic suggesting that no reaction occurs. This is in contrast to the reaction of other organic radicals with molecular oxygen which are highly exothermic, and these oxidation reactions are the principal sink for organic radicals in the environment [19,20].

Figure 4 depicts calculated Bader valence electron densities for *ortho*-semiquinone, *para*-semiquinone, phenoxyl, and phenyl radicals. These calculations were performed because it was felt that the reactivity of the radicals towards oxygen would be controlled by whether the unpaired electron was largely located on a carbon or oxygen atom. If the electron were located on a carbon center, then reaction with oxygen would result in a peroxide whereas reaction with an oxygen-centered site would result in a much less stable ozonide. Thus, carbon-centered radicals are expected be more reactive than oxygen-centered radicals. As one can see from the table, there is no difference between *o*-semiquinone and *p*-semiquinone while phenoxyl is slightly more carbon centered. (Phenyl, which has no oxygen, is of course primarily carbon centered.) These results suggest that phenoxyl may not be more reactive towards oxygen than semiquinone radicals. It is also consistent with experimental results in the literature that indicate molecular oxygen reacts with phenyl 10^5 cm^3/molecule-s faster than with phenoxyl at low temperatures [21,22].

In principal, the *g*-values of EPR spectra can be used to determine whether a radical is carbon-centered or oxygen-centered. As a general guide, the closer the unpaired electron is to an oxygen atom, the greater the *g*-value: for carbon- centered radicals *g*-values are <2.003 (i.e., for graphitic carbon, *g* = 2.0028 [23]; for a PAH radical, *g* ~2.0026 [24]). Carbon-centered radicals with an adjacent oxygen atom typically have higher *g*-values in the range of 2.003–2.004) [25], while for oxygen-centered radicals *g*-values are >2.004 [26]. However, these values can be shifted by matrix interactions or other substituents (e.g., chlorine [27]). In addition, if the unpaired electron is not exclusively centered on a single atom, the EPR spectrum is broadened. The structure of a PFR can also be altered by

interaction with a surface matrix, further shifting the EPR spectrum. These parameters are especially important in interpreting the results of the surface-mediated formation and stabilization of PFRs.

3.3. Surface-induced formation and stabilization of PFRs

Our experimental and theoretical studies indicate that resonance stabilized radicals will form and are sufficiently stable that they may undergo self-reaction in the gas-phase [28]. However, we already know that some radicals, when associated with surfaces, are stabilized and can exist, apparently, indefinitely [5].

We performed experiments in which 5% CuO on silica was used as a surrogate for combustion- generated fly-ash. Using a vacuum system and thermoelectric furnace, we dosed various possible radical precursors onto a surrogate surface at varying temperatures typical of that in the thermal and cool-zones of combustion systems [29]. The samples were then evacuated at 10^{-3} torr for 1 h to remove excess and physisorbed molecules, leaving only chemisorbed species.

FTIR studies of chemisorption of substituted phenols and chlorinated benzenes confirmed that they chemisorbed on the surfaces of transition metal oxides such as copper oxide under post-flame, cool-zone conditions [30]. X-ray spectroscopic studies using XANES spectroscopy indicated that Cu(II) was reduced in the course of the chemisorption process as a result of electron transfer between the molecule and site of chemisorption [31]. This electron transfer results in the formation of an organic radical associated with the surface [13].

Figure 5 summarizes the results of the EPR studies on these same samples. The dihydroxybenzenes, hydroquinone and catechol, formed stabilized radicals as low as 50–100 °C; however, their yield did not increase significantly with increasing temperature. The *g*-values remained relatively constant in the range of 2.006–2.007 as the dosing temperature was raised to 300 °C. In contrast, the chlorinated benzenes, chlorobenzene, and 1,2-dichlorobenzene, did not form radicals until 150 °C, but the radical yield increased dramatically by 225 °C. Their *g*-values were very high at low temperature, 2.007–2.008, before being reduced dramatically, 2.0045–2.0055, as the temperature increased. Phenol and 2-chlorophenol exhibited different behavior. Their *g*-values were low, 2.004–2.005, at low temperature and increased slightly with increasing temperature. In contrast to the other precursors, the yield of radicals from both phenol and 2-chlorophenol was low at low temperature but still relatively high at 300 °C. Based on these data, we believe that surface-associated PFRs may be formed as depicted in Fig. 6.

Initial chemisorption forms a surface-bound phenoxide by elimination of HCl for the chlorinated benzenes (chlorobenzene and 1,2 dichlorobenzene) and elimination of H_2O by the hydroxylated benzenes (phenol, hydoquinone, and catechol). In the case of 2-chlorophenol, which is both chlorine- and hydroxyl- substituted, chemisorption can occur by either route. Chlorobenzene, 1,2-dichlorobenzene, and phenol exhibit temperature-activated radical formation. However, the presence of a hydroxyl group in addition to another hydroxyl of chlorine substituent reduces the rate and yield of chemisorption (hydroquinone,

catechol, and 2-chlorophenol), presumably through strong hydrogen bonding that inhibits chemisorption. Based on yields, chlorine substitution, and hence HCl elimination, favors radical formation. Following chemisorption, electron transfer and reduction of the copper forms the surface-associated radical.

The *g*-values are also related to the degree of chlorine and hydroxy substitution. The chlorine-substituted radicals have the highest *g*-values at lower temperatures. However, they are dechlorinated with increasing temperature, thus reducing the *g*-values [32]. Consequently, chlorobenzene and 1,2-dichlorobenzene have high initial *g*-values that decrease with increasing temperature; whereas, hydroquinone and catechol exhibit intermediate, but constant, *g*-values. Phenol, which chemisorbs to form an unsubstituted phenoxyl radical, has a low *g*-value. 2-Chlorophenol, that can form a hydroxy- and a chlorine-substituted radical, exhibits an intermediate *g*-value that may be the superposition of hydroxy- and chlorine- substituted radicals.

Based on the current experimental evidence, there is little doubt that PFRs exist in combustion- generated particles and airborne fine particles. However, their exact origin, nature, mechanism of stabilization, reactions, and human health impacts must be the subject of considerable additional study before we fully understand or appreciate their environmental impacts.

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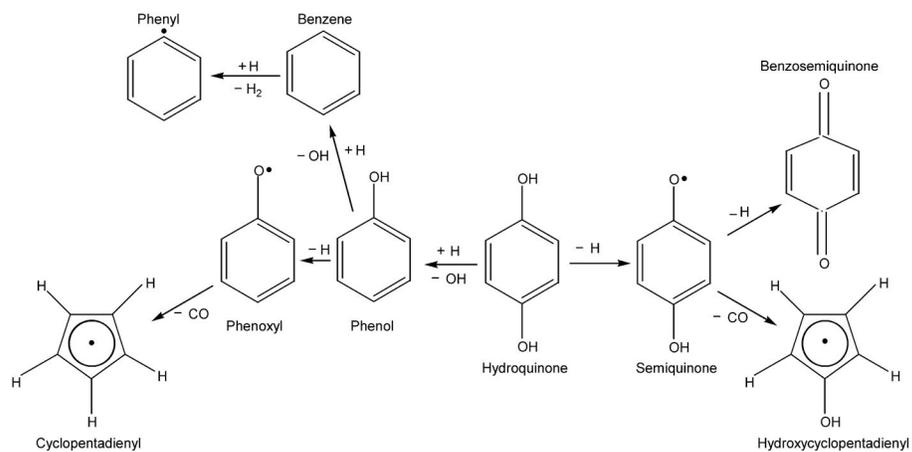
Fig. 1.
Pyrolytic decomposition pathways of hydroquinone that may result in various resonance stabilized radicals including *para*-semiquinone, phenoxyl, phenyl, hydroxycyclopentadienyl, and cyclopentadienyl as well as molecular products [33].
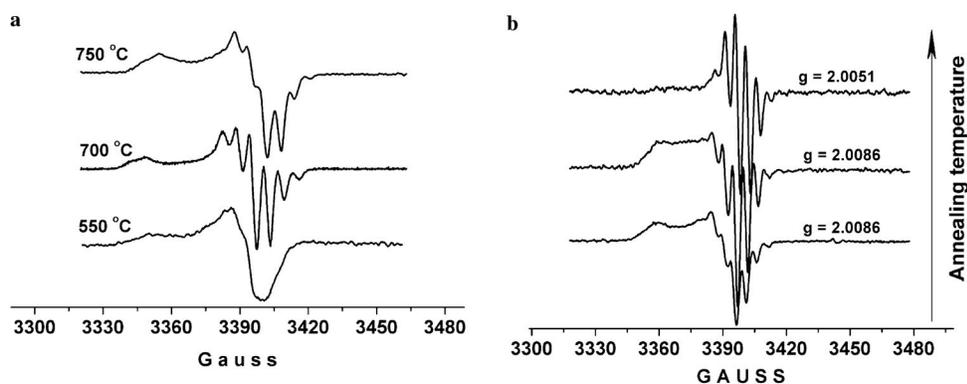
Fig. 2.
EPR spectra of radicals in a carbon dioxide matrix at 77 K from the pyrolysis of hydroquinone in carbon dioxide. (a) EPR spectra resulting from pyrolysis at various temperatures yielding multiple radicals. (b) Annealing of the sample obtained from 750 °C pyrolysis results in annihilation of some radicals and sharpening of the spectrum. The annealed spectrum obtained from pyrolysis of hydroquinone at 750 °C was identified as that of cyclopentadienyl. Qualitatively similar behavior was observed for catechol and phenol. All three samples yielded multiple radicals at low temperature and cyclopentadienyl at pyrolysis temperatures equal or higher than 750 °C.
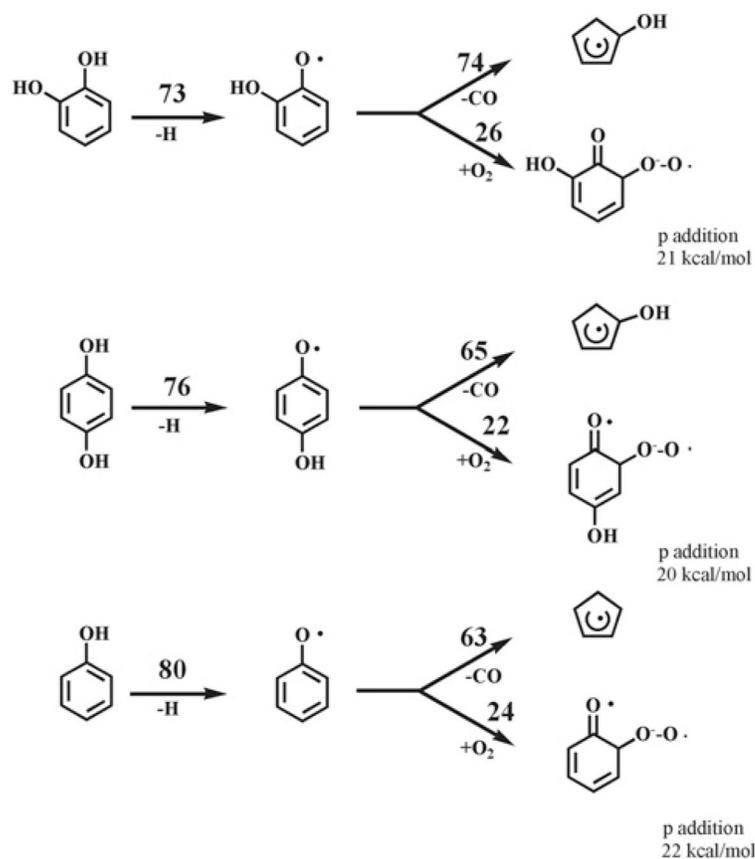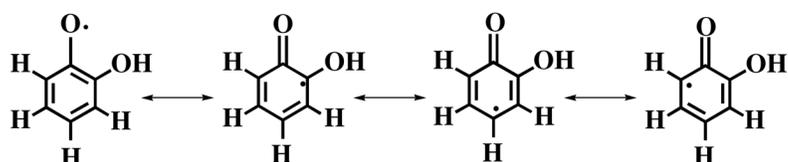
Fig. 3.
Activation energies (kcal/mol) for some energetically allowed reactions of *ortho*-semiquinone, *para*-semiquinone, and phenoxyl radical. Oxygen can add at the *para*- and *ortho*- positions but not the oxy radicals.

Radical	% C	% H	% O
o-semiquinone	52	11	37
p-semiquinone	50	13	37
phenoxyl	64	15	21
phenyl	82	18	na

Fig. 4.
Calculated Bader charge densities (%) for *ortho*-semiquinone (shown above), *para*-semiquinone, phenoxyl, and phenyl radicals. The greater the charge density of an atom, the more likely the unpaired electron resides on that atom.
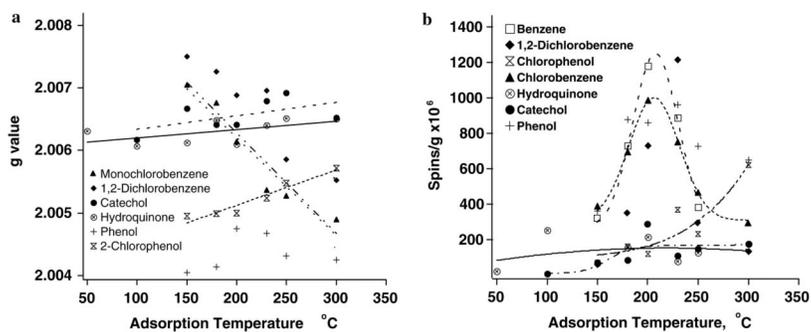
Fig. 5.
Temperature dependence of EPR *g*-values (a) and relative concentrations of radicals (b) formed from chemisorption of various precursors on a CuO/silica substrate. The observed radicals clearly fall into two groups: Type (I) resonance stabilized radicals of monochlorobenzene, 1,2 dichlorobenzene, and 2-chlorophenols that form in relatively high yields with a maximum near 200 °C and exhibit very high initial *g*-values that decrease with increasing temperature; and Type (II) semiquinone radicals of hydroquinone and catechol that form in lower yields at lower temperatures with yields that increase with increasing temperature and exhibit nearly constant *g*-values as a function of adsorption temperature.
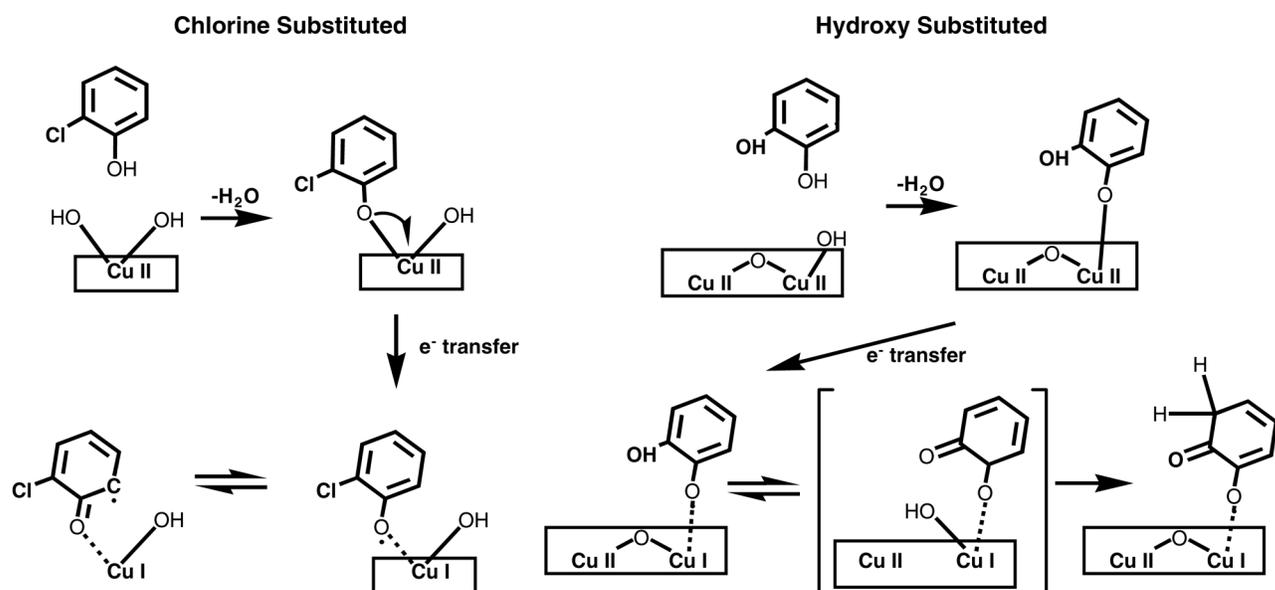
Fig. 6.
Proposed mechanism of chemisorption and radical formation of substituted benzenes (2-chlorophenol shown) on a copper oxide surface, and mechanisms of carbon or oxygen-centered radical formation based on chlorine or hydroxy substitution. Hydroxy-substituted phenols may persist as oxygen-centered radicals due reaction with neighboring surface oxide groups. Chlorine-substitution phenols may exist in a more carbon-centered mesomer due to the inductive effects of chlorine.