SUPPORTING INFORMATION FOR

Potential for Misidentification of Environmentally Persistent Free Radicals as Molecular Pollutants in Particulate Matter

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This material includes the EPR spectrum of the extracted EPFR of catechol in isopropyl alcohol, and proposed mechanistic pathways for formation of molecular products in from extraction of 6 different EPFRs in solution.

Figure 1 presents a representative EPR spectrum of the isopropyl alcohol extract of the CuO/silica samples exposed to catechol vapors. A weak, narrow EPR signal with a g value of 2.0051 was observed.

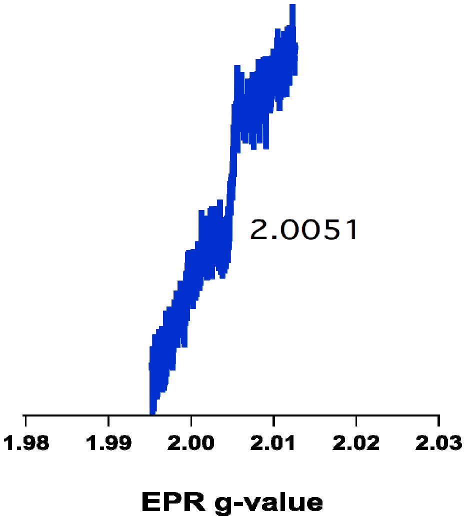
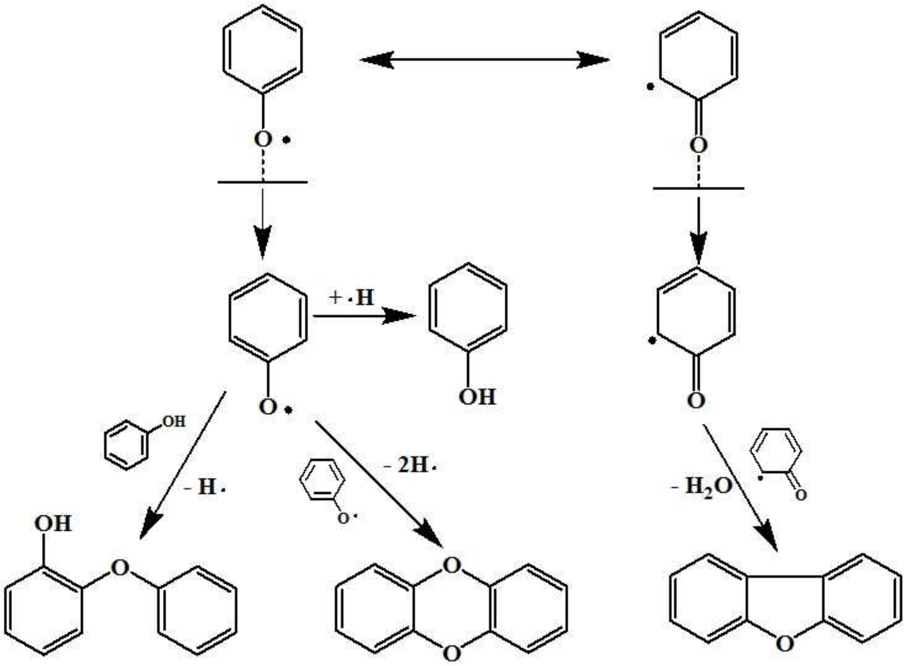


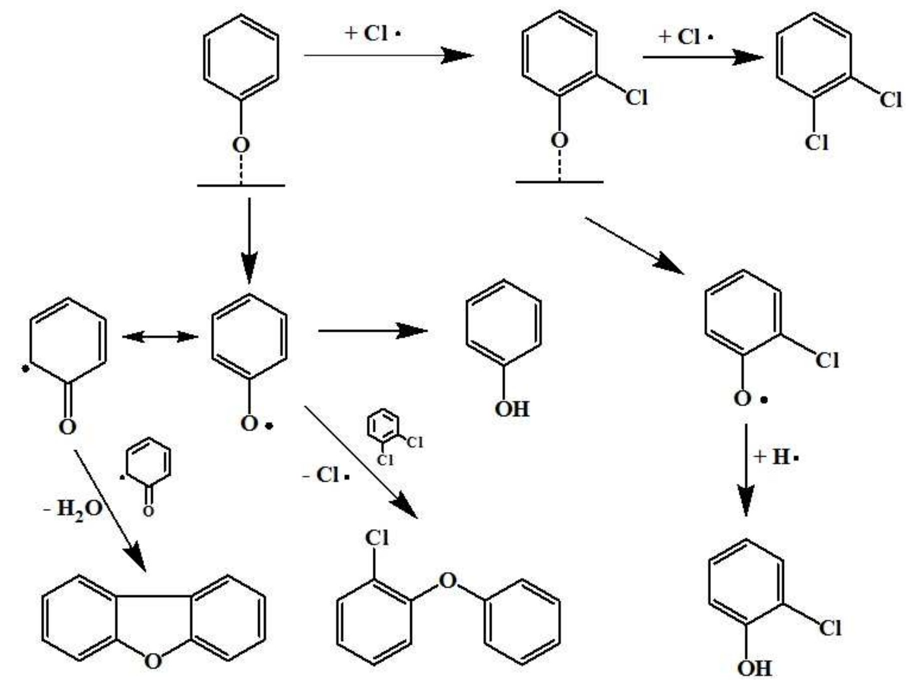
Figure 1: EPR spectra of the isopropyl alcohol extract of the radicals formed from the adsorption of catechol.

Scheme 1 presents pathways of formation of observed products upon the extraction of phenoxyl radicals formed by chemisorption of phenol. The surface-associated phenoxy radical may exist in both keto and enol forms (27). Dimerization of the enol- and keto-forms results in formation of dibenzo-p-dioxin and dibenzofuran, respectively. Abstraction of a solvent hydrogen by phenoxyl forms phenol. The radical-molecule reaction of phenoxyl with phenol forms hydroxydiphenyl ether.



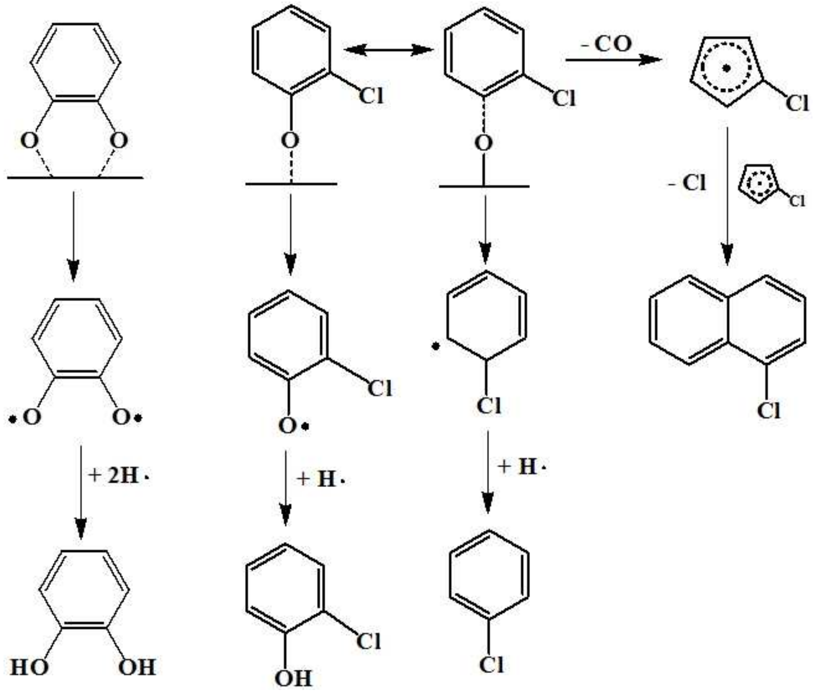
Scheme 1: Products of solution reaction of radicals extracted from chemisorbed phenol.

MCBz (cf. Scheme 2) reacts with the particle surface to form primarily chemisorbed phenoxyl radicals that form most of the same products observed from phenol. Surface-mediated chlorination, followed by phenoxyl-surface or phenoxyl-oxygen bond scission (with subsequent abstraction of a solvent hydrogen) form 2-MCP and 1,2-DCBz, respectively.



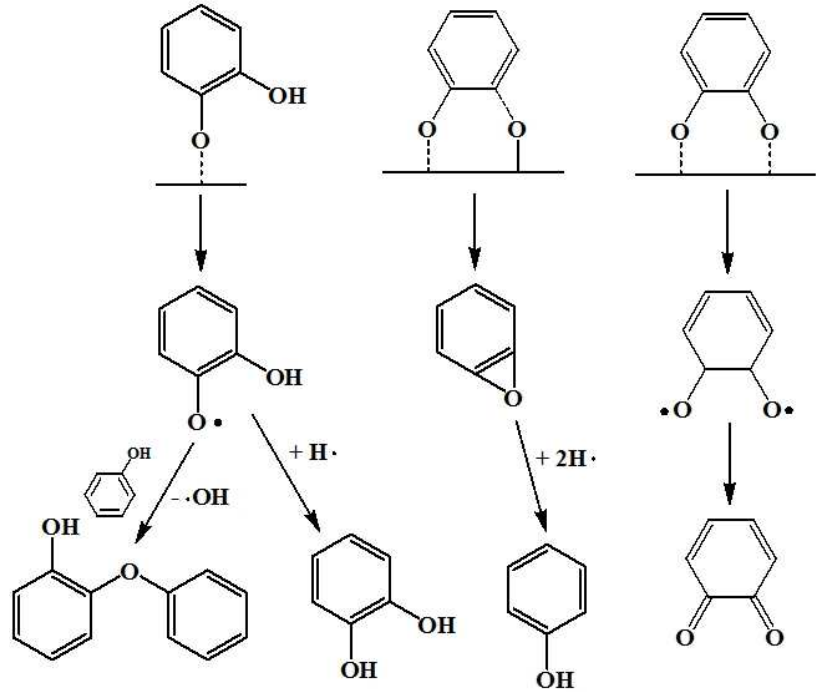
Scheme 2: Products of solution reaction of radicals extracted from chemisorbed MCBz.

Chemisorption of 1,2 DCBz (cf. Scheme 3) forms both 2-monochlorophenoxyl radical (via chemisorption at one site by HCl elimination) and a doubly surface-bound o-benzoquinone radical (via chemisorption at two sites by double HCl elimination). CT and 2-MCP are formed by hydrogen abstraction from the solvent by the o-semiquinone radical and 2-chlorophenoxyl radical, respectively. Chloronaphthalene is formed from recombination and rearrangement of chlorocyclopentadienyl radicals (formed by expulsion of CO from the 2-chlorophenoxyl radicals) in a pathway analogous to the gasphase formation of naphthalene from recombination of cyclopentadienyl radicals (36, 37). MCBz is formed by phenyl-oxygen bond scission and abstraction of a hydrogen from the solvent.



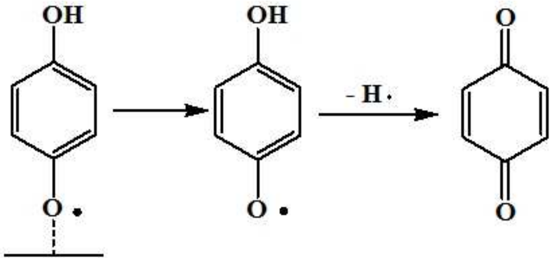
Scheme 3: Products of solution reaction of radicals extracted from chemisorbed 1,2-DCBz.

Similarly to 1,2-DCBz, CT (cf. Scheme 4) can also chemisorb at one or two sites via elimination of one or two H_2O's, respectively. In the case of CT, the chemisorpion is primarily via the doubly-bonded species, and solvent extraction of the surface associated o-benzoquinone radical is expectedly difficult, resulting in a very low yield of *o*-benzoquinone. CT is again formed from the extracted *o*-semiquinone radical via abstraction of a solvent hydrogen. Phenol is formed via an epoxide, formed by scission of one phenyl-oxygen bond and one oxygen-surface bond and hydrogen abstraction from the solvent. The singley-bound o-semiquinone extracted radical reacts with phenol to form hydroxydiphenyl ether.



Scheme 4: Products of solution reaction of radicals extracted from chemisorbed CT.

HQ chemisorbs via elimination of H_2O to form a surface-associated *p*-semiquinone radical. Upon extraction, it loses the second hydroxyl hydrogen to form exclusively *p*-benzoquinone. (cf. Scheme 5). Because of its rapid conversion to *p*-benzoquinone, dimerization products were not observed as was the case for the other extracted radicals.



Scheme 5: Products of solution reaction of radicals extracted from chemisorbed hydroquinone.