STM and FTIR Comparison of the Binding and Oxidation of Phenol Derivatives on Au(111)

Katherine M. Richard Final Seminar February 22, 1996

Reactions of organic molecules on surfaces are central to much of chemistry. Small molecule behavior at the solid-liquid interface is important in areas as diverse as fuel cells, environmental remediation, and corrosion protection. The behavior of Co [1] and CN^- [2] on surfaces has been well-characterized and there is interest in studying the behavior of larger and more relevant molecules.

This work has focused on the behavior of aromatic molecules on Au(111), including: 1) the binding and initial stages of oxidation of phenol, 2) the observation of surface poisoning during the continued oxidation of phenol and 2-naphthol, 3) the concentration and pH-dependent adsorption of uracil, and 4) the impact of ring substitution on the binding and reactivity of cyanophenols. These chemical systems have been studied using electrochemistry, surface infrared spectroscopy, and scanned probe microscopy.

Previous studies of phenol have indicated a potential-induced change in orientation [3] and the formation of passivating, polymeric films upon electro-oxidation [4,5]. UHV studies of phenol on Pt(111) indicate the formation of a (3 x 3) overlayer with the phenol ring parallel to the surface [6]. In solutions with a pH > 10, phenol is deprotonated and the polymerization reaction proceeds with few side products [7]. Voltammetric studies have shown that substituting a CN group at ring position 2 or 4 inhibits the electro-oxidation of the molecule while substitution at the 3 position does not (see Figure 1). The observed inhibition of oxidation is due to two factors [8]: 1) blocking of preferred polymerization sites, as phenol is known to polymerize through the *ortho* and *para* positions on the ring; 2) electronic effects from the presence of a strongly electron-withdrawing group *ortho* or *para* to the OH group, which stabilizes the anion form of the molecule.

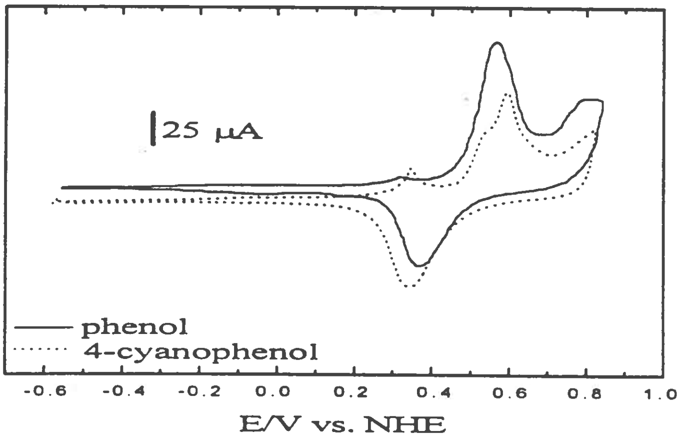

Figure 1. CV of Au(111) in solutions containing 0.1 M NaOH and added organics.

The surface FTIR spectra of phenol, 3-cyanophenol, and 4-cyanophenol are shown in Figure 2. Phenol and 4-cyanophenol display both positive- and negative-features, while no bands are observed for 3-cyanophenol. The positive-features for both phenol and 4-cyanophenol can be attributed to asymmetric ring modes. These modes are symmetry forbidden in the solution species of the molecule. A reduction in the symmetry of the system ($C_2 \rightarrow C_s$) occurs upon adsorption, which allows the asymmetric ring modes to display intensity. The negative-feature is due to loss of intensity of the aryl-O stretch as the molecules tilt away from the surface normal.

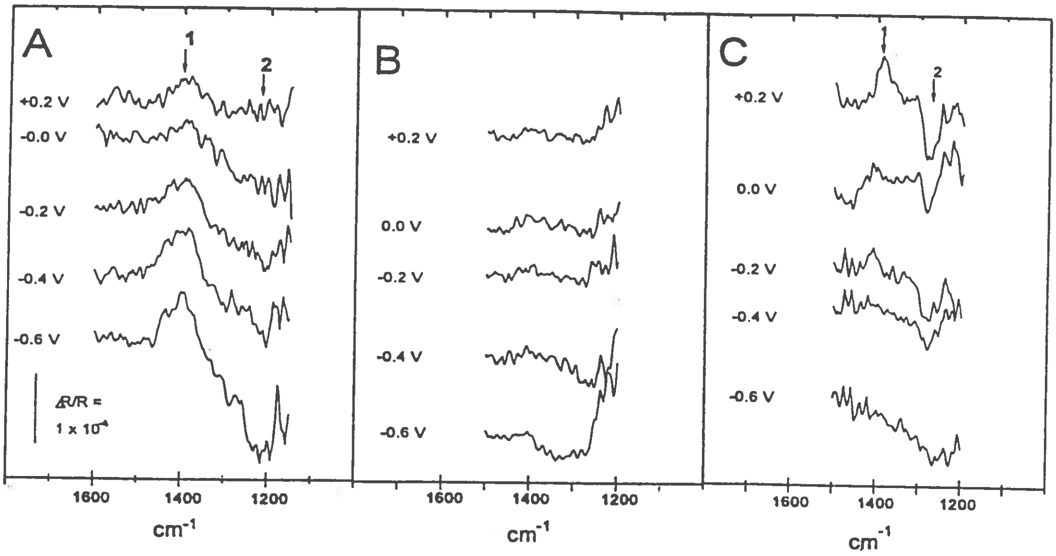

Figure 2. Surface FTIR spectra of A) phenol, B) 3-cyanophenol, C) 4-cyanophenol

The lack of observable bands for 3-cyanophenol indicates that the molecule is orienting to the electrode surface in a different way than phenol and 4-cyanophenol. The molecule may be oriented with the ring parallel to the surface or in a disordered fashion. STM investigations provide additional information about the structure of adlayers.

Phenoxide has been shown to adopt a (√3 x √3)R30° overlayer structure on Au(111) [9], as shown in Figure 3A. When the potential is briefly swept into the region of phenol oxidation, oligomers of phenol form on the Au(111) surface (Figure 3C). These oligomers have limited chain length due to close-packing among the molecules on the surface, which limits the approach of other monomers.

STM studies in solutions containing cyanophenols display the known surface reconstruction for Au(111) [10], even at potentials which the voltammetry indicates the cyanophenols are associated with the surface. This indicates that the cyanophenols are only weakly bound to the electrode surface [11]. As the potential is swept positive, 4-cyanophenol adopts a structure similar to that observed for phenol, while 3-cyanophenol never displays an ordered overlayer structure.

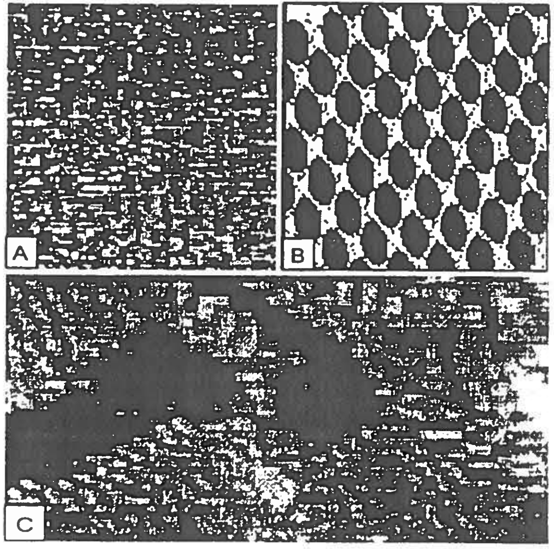

Figure 3. A) STM image of the (√3 x √3)R30° phenoxide overlayer on Au(111); B) A model of the overlayer. Ovals represent phenoxide, open circles represent Au(111); C) STM image of oligomers of phenol Au(111) formed by electro-oxidation.

Computer modeling of the adlayers structures shows that the (√3 x √3)R30° overlayer structure is close-packed for phenol and 4-cyanophenol. The presence of the CN group at ring position 3 creates steric repulsions between the molecules, preventing the formation of the (√3 x √3)R30° adlayer. Packing between rings has been shown to be important in the formation of ordered adlayers [12]. As the steric hindrance drives the molecules apart, less packing can occur between rings and there is inherently less order in the overlayer.

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