

Heterogeneous and Photochemical Reactions of Solid Benzophenone–Catechol Films with NO₂[†]

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Solid–air interfaces are ubiquitous to the atmosphere, and heterogeneous reactions between gaseous oxidants and surface adsorbed organics on these interfaces can impact tropospheric chemistry. Solid benzophenone–catechol films serve as model photosensitizer–polyphenol compounds that we reacted with NO₂ in the parts-per-billion range under dark and light conditions at 300 K and 20% relative humidity. Attenuated total reflectance infrared spectroscopy (ATR-FTIR) monitored chemical changes in the organic film during these reactions to directly identify condensed-phase products. Catechol, when mixed with benzophenone or dicyclohexyl ketone, reacted with NO₂ under dark conditions, forming 4-nitrocatechol as the exclusive condensed-phase product; pure catechol films did not react. Kinetic isotope experiments found $\text{rate}[\text{C}_6\text{H}_4(\text{OH})_2]/\text{rate}[\text{C}_6\text{H}_4(\text{OD})_2] = 3.3 \pm 0.5$, indicating that breaking an O–H bond was critical to the rate-determining step. A mechanism involving the *ortho*-semiquinone radical, possibly stabilized by hydrogen bonding to the coadsorbed ketone, is discussed. The reaction was also found to be second order (2.09 ± 0.18) with respect to NO₂, suggesting a possible pre-equilibrium with N₂O₄. Although benzophenone is a well-known photosensitizer, the rate of 4-nitrocatechol formation was not enhanced by UV-A/visible radiation. This observation eliminates this pathway as a possible photoenhanced daytime source of HONO. However, ATR-FTIR detected additional photochemical products resulting from a photoinitiated reaction between benzophenone and 4-nitrocatechol. These results highlight the potential for heterogeneous chemistry involving surface adsorbed organics to form nitroaromatic compounds, which are of interest due to their phytotoxic and UV absorbing properties.

I. Introduction

Airborne particulate and ground level surfaces (e.g., soils, buildings) provide unique solid–air interfaces that can support heterogeneous chemistry and impact tropospheric photochemical cycles.¹ A complete understanding of these solid–air interfaces, however, requires the inclusion of heterogeneous and photochemical reactivity of surface adsorbed organics.² For instance, sea salt³ and mineral^{4,5} aerosols acquire organic coatings during formation processes and from adsorption of semivolatile compounds during transport. Both biogenic and anthropogenic emissions (from sources such as vegetation and combustion) generate organic aerosols and contribute to the organic content of inorganic aerosols.^{6–9} Urban surfaces, such as buildings and windows, also contain surface films composed of complex mixtures of organic and inorganic compounds,¹⁰ whereas rural surfaces such as soils are rich in degraded biomolecules.¹¹ These surface adsorbed organics may alter the physical and chemical properties of these atmospherically relevant interfaces.^{12–14}

Interest in adsorbed organics initially focused on water uptake since organic films might impact an aerosol's ability to act as cloud condensing nuclei, thereby altering the earth's radiative balance.^{15,16} Saxena et al. found that organics can increase water absorption by water-soluble inorganic aerosols in rural environments, but an opposite effect was noted for organics in urban air masses.¹⁷ The difference in these environments was attributed to the hydrophobic versus hydrophilic nature of the organic films. Chemical processing of organic films, through heteroge-

neous reactions with atmospheric radicals, may alter their hydrophobic nature through oxidation.¹⁸ For instance, the oxidation of fatty acids, predominately on oleic acid, which is ubiquitous to the troposphere, serves as a principal laboratory model for understanding the chemical processing of organic coatings (e.g., see refs 13 and 19 and references therein). Characterization of atmospheric aerosols by Russel and co-workers using soft X-ray spectromicroscopy identified shorter-chain, more oxygenated organics on the surface relative to the interior, providing experimental support for such chemical processing in the troposphere.²⁰

More recently, laboratory studies have demonstrated that humic acid films and aerosols photochemically reduce nitrogen dioxide to nitrous acid, HONO, providing a potential pathway to explain a missing daytime source of HONO.^{21,22} This is of particular interest given the importance of humic and fulvic acids in soils¹¹ and the extent of humic-like substances (HULIS) in the troposphere.²³ Additional flow-tube experiments also observed the photochemical reduction of NO₂ to HONO on small organic compounds.²⁴ Mixtures containing a photosensitizer, such as aromatic ketones, and an electron donor, such as phenols, were especially effective at generating HONO under photochemical conditions. These experiments, however, focused exclusively on the gas phase reactants and products. The investigations described below complement these prior studies using attenuated total reflectance infrared spectroscopy to monitor the organic films under similar dark and photochemical conditions.

Attenuated total reflectance infrared spectroscopy (ATR-FTIR) provides a technique for monitoring condensed-phase species involved in heterogeneous chemistry with gaseous

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