

# Heterogeneous reactions of surface-adsorbed catechol with nitrogen dioxide: substrate effects for tropospheric aerosol surrogates†

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Received 1st February 2010, Accepted 21st June 2010

DOI: 10.1039/c002079f

Surface-adsorbed organics can alter the chemistry of tropospheric aerosols thereby impacting photochemical cycles and altering aerosol properties. The nature of the surface can also influence the chemistry of the surface-adsorbed organic. We employed diffuse reflectance infrared spectroscopy (DRIFTS) to monitor the adsorption of gaseous catechol on several tropospheric aerosol surrogates and to investigate the subsequent reactivity of adsorbed catechol with nitrogen dioxide. The dark heterogeneous reaction of NO<sub>2</sub> with NaCl-adsorbed catechol produced 4-nitrocatechol, 1,2-benzoquinone, and the ring-cleaved product muconic acid, with product yields of 88%, 8%, and 4% at relative humidity (RH) < 2%, respectively. The reaction was first-order with respect to both catechol and NO<sub>2</sub>. The reactive uptake coefficient for NO<sub>2</sub> + NaCl-adsorbed catechol increased from  $3 \times 10^{-6}$  at <2% RH to  $7 \times 10^{-6}$  at 30% RH. These reactions were more than two orders of magnitude more reactive than NaCl without adsorbed catechol. The 4-nitrocatechol product yield was enhanced on NaF, while NaBr-adsorbed catechol produced considerably more 1,2-benzoquinone and muconic acid. This substrate effect is discussed in terms of each substrate's ability to polarize the phenol group and hinder hydrogen atom abstraction from intermediate *o*-semiquinone radicals. These dark heterogeneous reactions may alter the UV-visible absorbing properties of tropospheric aerosols and may also contribute as a dark source of NO<sub>2</sub><sup>-</sup>/HONO. These results contrast prior observations which found pure catechol thin films unreactive with NO<sub>2</sub>, highlighting the need to specifically consider substrate and matrix effects in laboratory systems.

## 1. Introduction

Tropospheric aerosols impact atmospheric chemistry, Earth's radiative balance, and human health. Many critical questions regarding the environmental and health impacts of these aerosols remain unanswered because of their diverse and complex chemical compositions, which often vary with transport *via* chemical weathering.<sup>1–3</sup> Efforts to resolve these issues involve field measurements, laboratory experiments, and atmospheric simulations. Of interest here, laboratory experiments typically rely on simplified model systems to investigate the chemical and/or physical properties of individual components identified in field studies. As laboratory models become increasingly complex to better model tropospheric conditions, the importance of matrix and substrate effects has emerged.<sup>4,5</sup>

Organics comprise a significant fraction of tropospheric aerosols.<sup>6–10</sup> In addition to primary and secondary organic aerosols, thin films and adsorbed organics are ubiquitous to non-organic aerosols—such as sea salt, mineral, carbonaceous and sulfate particles.<sup>11–13</sup> Surface-adsorbed organics can alter the chemistry of these interfaces, thereby impacting

tropospheric photochemical cycles<sup>14,15</sup> and altering aerosol properties.<sup>16–18</sup> The nature of the surface can also influence the chemistry of the surface-adsorbed organics.

Li and coworkers investigated the adsorption of aldehydes and ketones on mineral oxides.<sup>19</sup> Adsorption on SiO<sub>2</sub> was reversible, while basic and acidic oxides, such as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and CaO, supported irreversible uptake and subsequent aldol condensation reactions.<sup>19</sup> For heterogeneous systems involving a trace gas reacting with an adsorbed species, a dominant substrate effect results from the Langmuir–Hinshelwood mechanism.<sup>20</sup> In this scenario, adsorption of the gaseous reactant precedes reactivity with surface-bound species. Thus, surfaces that partition a greater concentration of gaseous reactant to the adsorbed phase exhibit higher uptake coefficients. For instance, the oxidation of benzo[*a*]pyrene by ozone exhibited the highest reactivity when adsorbed on soot followed by azelaic-acid aerosols, and was unreactive on NaCl.<sup>4,21</sup> Similar substrate effects were observed for the ozonolysis of surface-bound anthracene<sup>22</sup> and oleic acid.<sup>23</sup>

The present study expands on this prior work by investigating the chemistry of catechol adsorbed on carbonaceous, mineral, and sea salt aerosol surrogates. Phenols have been identified as a significant organic functional group in aerosols derived from the marine environment.<sup>24</sup> Therefore, catechol was chosen as a model polyphenol compound to understand the potential heterogeneous chemistry of this organic fraction. Catechol is also a major lignin pyrolysis product present in biomass combustion smoke, accounting for up to 1.8% of the total resolved organic content in conifer smoke.<sup>25,26</sup> We observed

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† Electronic supplementary information (ESI) available: Fig. S1 shows results of exposing NaBr-adsorbed products to H<sub>2</sub><sup>18</sup>O. Fig. S2 reports spectra of kaolinite-adsorbed catechol and products. Fig. S3 depicts exponential decay of NaCl-adsorbed catechol due to the reaction with NO<sub>2</sub>. Fig. S4 shows effect of RH on the rate of reaction for NaBr-adsorbed catechol + NO<sub>2</sub>. See DOI: 10.1039/c002079f