Supplemental Information

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

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Figure SI-1. Isotope experiment using H$_2^{18}$O. (a) Spectrum of NaBr-adsorbed catechol (i.e., $t=0$ minutes). (b) Spectrum of NaBr adsorbed products after exposure to NO$_2$ at RH <2%. (c) Spectrum of NaBr-adsorbed products after stopping NO$_2$ flow, then exposing sample to H$_2^{18}$O. A similar experiment is shown in Figure 4 of the paper using H$_2^{16}$O. In this Figure, the 1687 cm$^{-1}$ peak in (b), corresponding to 1,2-BQ, disappears concurrent with the formation of two peaks in (c) at 1732 and 1703 cm$^{-1}$, which are assigned to C=^{16}O and C=^{18}O stretching vibrations for MA. These results demonstrate the incorporation of water with 1,2-BQ eventually forming MA.

Figure SI-2. (a) Spectrum of kaolinite-adsorbed catechol at RH <2%. Strong kaolinite lattice vibrations absorb IR radiation below 1280 cm$^{-1}$ obscuring vibrations for absorbed species. (b) Spectra of absorbed products recorded at $t=40$ and 160 minutes for the reaction of kaolinite-adsorbed catechol + 101 ppb NO$_2$ at RH <2%. Dominant product peaks correspond to 4-NC, while a minor shoulder at 1662 cm$^{-1}$ is attributed to 1,2-BQ. The absence of a peak at 1743 cm$^{-1}$ suggests very little MA.
Figure SI-3. Integrated rate law plots for the decay of NaCl-adsorbed catechol, monitored by the integrated area of the peak at 1097 cm$^{-1}$ (circles), for the reaction with 80 ppb NO$_2$ at RH <2%. Red lines show exponential (left) and linear (middle, right) fits to the data indicating first-order reaction with respect to surface-adsorbed catechol.

Figure SI-4. Percent abundance as a function of time and RH for NaBr-adsorbed catechol + 80 ppb NO$_2$. (See text for discussion about product yield determinations.) Increasing RH caused the rate of 4-NC formation to decrease by a factor of three. Adsorbed water further hindered the hydrogen atom transfer necessary for 1,2-BQ and MA formation, causing a more significant decrease in their formation rates.