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Supplemental Information

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

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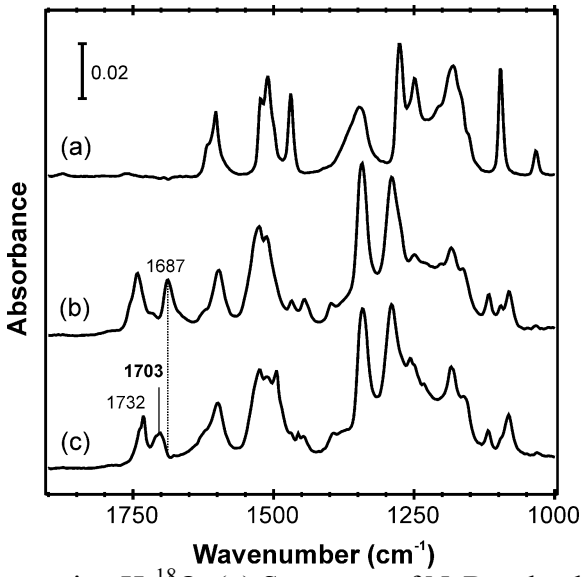

Figure SI-1. Isotope experiment using $H_2{}^{18}O$. (**a**) Spectrum of NaBr-adsorbed catechol (i.e., $t = 0$ minutes). (**b**) Spectrum of NaBr adsorbed products after exposure to NO_2 at RH <2%. (**c**) Spectrum of NaBr-adsorbed products after stopping NO_2 flow, then exposing sample to $H_2{}^{18}O$. 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.

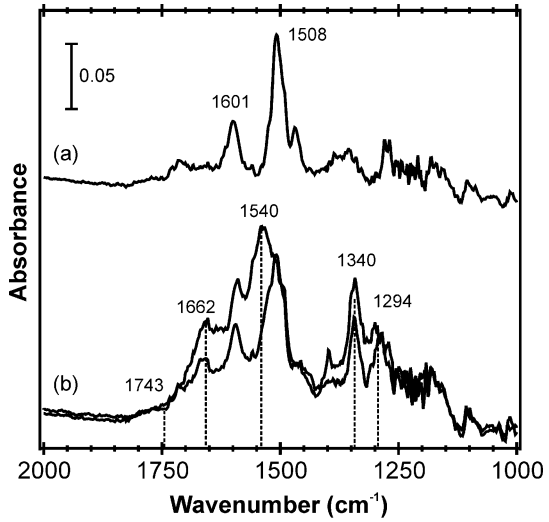

Figure SI-2. (**a**) Spectrum of kaolinite-adsorbed catechol at RH <2%. Strong kaolinite lattice vibrations absorb IR radiation below 1280 cm^{-1} obscuring vibrations for absorbed species. (**b**) Spectra of absorbed products recorded at $t = 40$ and 160 minutes for the reaction of kaolinite-adsorbed 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.

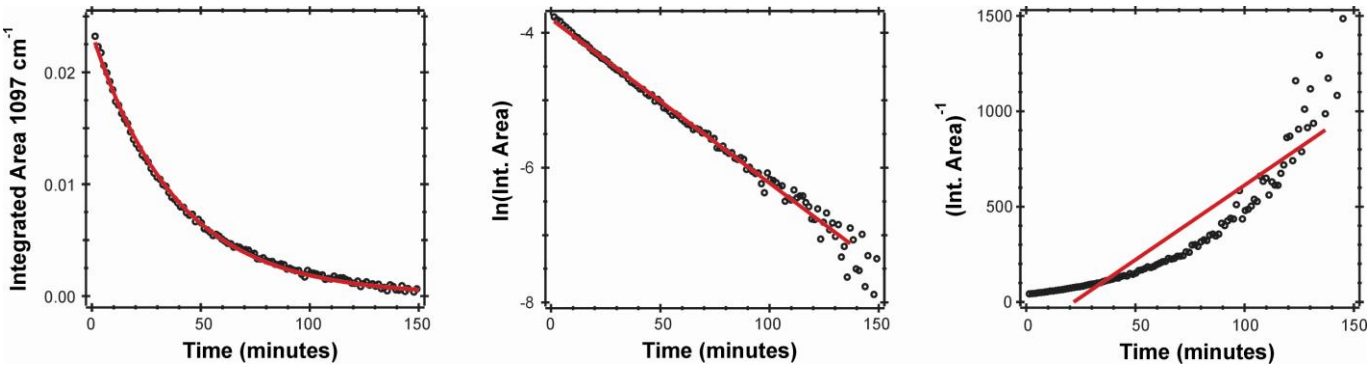

Figure SI-3. Integrated rate law plots for the decay of NaCl-adsorbed catechol, monitored by the integrated area of the peak at 1097 cm^{-1} (circles), for the reaction with 80 ppb NO_2 at RH <2%. Red lines show exponential (left) and linear (middle, right) fits to the data indicating first-order reaction with respect to surface-adsorbed catechol.

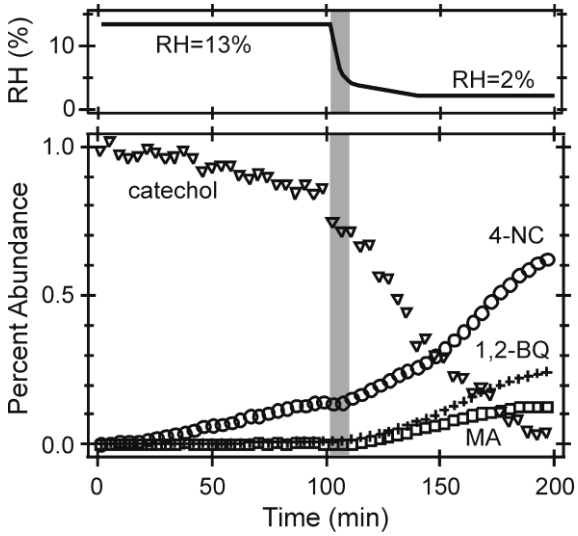

Figure SI-4. Percent abundance as a function of time and RH for NaBr-adsorbed catechol + 80 ppb NO_2. (See text for discussion about product yield determinations.) Increasing RH caused the rate of 4-NC formation to decrease by a factor of three. Adsorbed water further hindered the hydrogen atom transfer necessary for 1,2-BQ and MA formation, causing a more significant decrease in their formation rates.