Production of molecular iodine from the heterogeneous reaction of nitrogen dioxide with solid potassium iodide

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Molecular iodine impacts tropospheric chemistry, especially in coastal regions of the marine boundary layer where iodine bursts correlate with ultrafine particle formation. Although biogenic sources dominate coastal I$_2$ release, inorganic heterogeneous chemistry may also contribute to the global iodine budget. We investigated the heterogeneous chemistry of NO$_2$/N$_2$O$_4$ with solid KI, a component of dehydrated sea salt aerosol, and identified I$_2$(g) as the major gaseous product. Diffuse reflectance infrared spectroscopy and ion chromatography identified nitrite as the major condensed-phase product for the reaction of KI(s) + NO$_2$(g) ($5.4 \times 10^{13}$ to $2.0 \times 10^{15}$ molecules cm$^{-3}$) at relative humidities between 2% and 30%. The reaction was second order with respect to NO$_2$, suggesting that N$_2$O$_4$ was the reactive species. Reactive uptake coefficients, calculated with respect to [N$_2$O$_4$], were independent of relative humidity with an average value of $\gamma_{\text{BET}} = (6.1 \pm 0.3) \times 10^{-4}$. Concurrent gas phase UV-visible spectroscopy indentified I$_2$(g) production with near stoichiometric release corresponding to 2 KI(s) + N$_2$O$_4$(ads) $\rightarrow$ 2 KNO$_2$(s) + I$_2$(g). Condensed-phase nitrate was also identified at high [N$_2$O$_4$] and low RH, which was attributed to the oxidation of product KNO$_2$ by gaseous NO$_2$/N$_2$O$_4$. The heterogeneous chemistry of ozone with aqueous iodide has previously been considered as a source of molecular iodine in the marine boundary layer. These results suggest that the heterogeneous chemistry between NO$_2$/N$_2$O$_4$ and iodide deserves further consideration as a nonbiogenic source of molecular iodine.