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

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[1] 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_2O_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 $KI(s) + NO_2(g)$ (5.4×10^{13} to 2.0×10^{15} molecules cm^{-3}) at relative humidities between 2% and 30%. The reaction was second order with respect to NO_2, suggesting that N_2O_4 was the reactive species. Reactive uptake coefficients, calculated with respect to $[N_2O_4]$, were independent of relative humidity with an average value of $\gamma_{BET} = (6.1 \pm 0.3) \times 10^{-4}$. Concurrent gas phase UV-visible spectroscopy indentified $I_2(g)$ production with near stoichiometric release corresponding to $2\ KI(s) + N_2O_4(ads) \rightarrow 2\ KNO_2(s) + I_2(g)$. Condensed-phase nitrate was also identified at high $[N_2O_4]$ and low RH, which was attributed to the oxidation of product KNO_2 by gaseous NO_2/N_2O_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_2O_4 and iodide deserves further consideration as a nonbiogenic source of molecular iodine.

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