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Hydroxyl radical reactivity at the air-ice interface

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Abstract. Hydroxyl radicals are important oxidants in the atmosphere and in natural waters. They are also expected to be important in snow and ice, but their reactivity has not been widely studied in frozen aqueous solution. We have developed a spectroscopic probe to monitor the formation and reactions of hydroxyl radicals in situ. Hydroxyl radicals are produced in aqueous solution via the photolysis of nitrite, nitrate, and hydrogen peroxide, and react rapidly with benzene to form phenol. Similar phenol formation rates were observed in aqueous solution and bulk ice. However, no reaction was observed at air-ice interfaces, or when bulk ice samples were crushed prior to photolysis to increase their surface area. We also monitored the heterogeneous reaction between benzene present at air-water and air-ice interfaces with gas-phase OH produced from HONO photolysis. Rapid phenol formation was observed on water surfaces, but no reaction was observed at the surface of ice. Under the same conditions, we observed rapid loss of the polycyclic aromatic hydrocarbon (PAH) anthracene at air-water interfaces, but no loss was observed at air-ice interfaces. Our results suggest that the reactivity of hydroxyl radicals toward aromatic organics is similar in bulk ice samples and in aqueous solution, but is significantly suppressed in the quasi-liquid layer (QLL) that exists at air-ice interfaces.

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