

Meeting at the Interface

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Reactions within or on the surfaces of liquid or solid particles are known to play an important role in the stratosphere, the atmospheric layer from about 10 to 50 kilometers above Earth's surface. Much less is known about such heterogeneous chemistry in the troposphere, the

layer from Earth's surface up to the stratosphere. What little is known has focused on the ubiquitous aqueous droplets, which have generally been assumed to function as well-mixed microscopic chemical reactors. But this view is likely too simplistic. On page 301, Knipping *et al.* (1) use a combination of laboratory experiments, kinetic modeling, and molecular dynamics simulations to show that reactions at the droplet surface may also contribute in an important way to tropospheric heterogeneous chemistry.

There is an enormous variety of tropospheric surfaces, ranging from sea salt, mineral dust, and combustion-generated aerosols to Earth's surface itself. Together with the bewildering array of gas-phase species in the troposphere, this leads to a wide range of potential heterogeneous interactions. Knowledge of tropospheric heterogeneous chemistry is almost certainly incomplete, but some key processes have been identified. These include conversion of NO_x ($\text{NO} + \text{NO}_2$) to HNO_3 by the reaction of N_2O_5 with moist aerosols (2) and heterogeneous hydrolysis of N_2O_5 to form nitrous acid (HONO) (3). Photochemical production of formaldehyde at the air-snow interface constitutes an important local HCHO source in Arctic surface air (4). Recently, it has been speculated that mineral dust, long believed to be a nonreactive substrate, can interact with N_2O_5 , O_3 , and HO_2 radicals to influence gas-phase chemistry (5).

Despite its benign source, sea salt aerosol has proved to be a surprisingly complex and interactive tropospheric chemical constituent. It has been recognized for some time that HCl volatilizes from sea salt aerosols as a result of displacement by strong acids, such as HNO_3 or H_2SO_4 gases (6). More recently, a combination of atmospheric measurements, laboratory experiments, and kinetic simulations has shown that reactive chlorine-containing gases (Cl_2 , HOCl , ClNO_2 , and ClBr) may be released from sea salt aerosols by heterogeneous processes (7, 8). Episodic destruction of boundary layer ozone in the Arctic has been attributed to catalytic cycles involving BrO radicals (9, 10). Satellite observations show

that tropospheric air masses enriched in BrO are always situated close to sea ice, supporting the hypothesis that autocatalytic release of bromine from sea salt gives rise to substantial BrO formation (11). During halogen liberation from sea salt, gaseous Cl_2 is generated from aqueous sea salt particles in the presence of gas-phase hydroxyl (OH) radicals (12). The generation of molecular chlorine was presumed to be a result of the interaction of gas-phase OH radicals with the brine solution, but the observed rate of Cl_2 production could not be explained on the basis of known bulk aqueous-phase chemistry. There is evidence that large, polarizable anions preferentially concentrate at the surface of aqueous solutions of inorganic salts, in contrast to small, nonpolarizable cations, which remain in the bulk of the solution phase (13). Knipping *et al.* (1) performed molecular dynamics simulations of $\text{NaCl-H}_2\text{O}$ mixtures to investigate to what extent this effect also occurs in seawater and whether this might explain the generation of Cl_2 . Their results show that the large chloride anions indeed congregate

at the surface more readily than the small sodium cations, which snuggle comfortably in the hydrogen-bonded water structure. Recent evidence from Monte Carlo simulations indicates that this phenomenon also occurs with hydronium ions in water (see the figure).

With chloride ions predicted to occupy a substantial fraction of the sea salt aerosol surface, incoming gas-phase OH radicals can encounter Cl^- ions to form a surface OH-Cl^- complex, which is then assumed to undergo either self-reaction or decomposition. The self-reaction releases molecular chlorine to the gas phase. When the rates of self-reaction and decomposition of the complex are adjusted to fit experimental data, the observed rate of laboratory production of molecular chlorine can be reproduced by this mechanism (1). Moreover, the

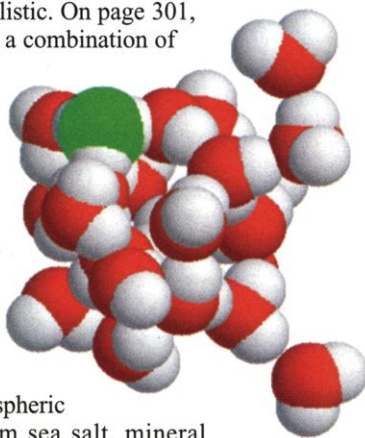
resulting concentration of Cl atoms falls in the right range when compared with ambient data, namely about 10^4 to 10^5 molecules/ cm^3 .

Other highly concentrated inorganic salt particles are also ubiquitous in the atmosphere. Aerosol sulfates and nitrates, together with their associated cations and water, constitute the largest category, by mass, of inorganic anthropogenic particulate matter. It is known that such particles exert a radiative effect on climate, but from a chemical point of view they have

generally been assumed to function simply as reservoirs for their gaseous molecular counterparts. Do ionic surface enrichment mechanisms also occur in such particles? If so, what are the implications for gas-phase tropospheric chemistry? These questions will likely receive serious attention in the laboratories of atmospheric and aerosol chemistry for some time to come.

References and Notes

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15. I thank I. Kusaka and D. Oxtoby for providing the figure.



Monte Carlo simulation of a cluster of water molecules and one hydronium (H_3O^+) ion.

This simulation, performed by Isamu Kusaka and David Oxtoby of the University of Chicago, uses the polarizable model potentials for hydronium ion and a water molecule proposed by Kozack and Jordan (14). In the model, the hydronium ion and the water molecule each carry a single isotropic polarizability. The simulation used a spherical cell with a radius of 30 Å, centered around the oxygen site of the hydronium ion and containing 22 water molecules. The hydronium ion prefers the surface of the cluster because it cannot be incorporated easily into the hydrogen bond network of the water molecules. The preferential surface migration is probably caused by the mismatch in H-O-H bond angles, rather than the size of the ion itself.