

CHEMICAL REACTIONS AT AQUEOUS INTERFACES

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...: dedicated to my family :...
ccclskk

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ABSTRACT

Interfaces or phase boundaries are a unique chemical environment relative to individual gas, liquid, or solid phases. Interfacial reaction mechanisms and kinetics are often at variance with homogeneous chemistry due to mass transfer, molecular orientation, and catalytic effects. Aqueous interfaces are a common subject of environmental science and engineering research, and three environmentally relevant aqueous interfaces are investigated in this thesis: 1) fluorochemical sonochemistry (bubble-water), 2) aqueous aerosol ozonation (gas-water droplet), and 3) electrolytic hydrogen production and simultaneous organic oxidation (water-metal/semiconductor). Direct interfacial analysis under environmentally relevant conditions is difficult, since most surface-specific techniques require relatively ‘extreme’ conditions. Thus, the experimental investigations here focus on the development of chemical reactors and analytical techniques for the completion of time/concentration-dependent measurements of reactants and their products. Kinetic modeling, estimations, and/or correlations were used to extract information on interfacially relevant processes.

We found that interfacial chemistry was determined to be the rate-limiting step to a subsequent series of relatively fast homogeneous reactions, for example: 1) Pyrolytic cleavage of the ionic headgroup of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) adsorbed to cavitating bubble-water interfaces during sonolysis was the rate-determining step in transformation to their inorganic constituents CO, CO₂, and F⁻; 2) O_{3(g)} oxidation of I_(aq)⁻ to HOI_(aq) at the aerosol-gas interface is the rate-determining step in the oxidation of Br_(aq)⁻ and Cl_(aq)⁻ to dihalogens; 3) Electrolytic formation of >TiOH• groups at the BiO_x-TiO₂/Ti anode is rate-limiting for the overall

oxidation of organics by the dichloride radical, $\text{Cl}_2^{\bullet-}$. We also found chemistry unique to the interface, for example: 1) Adsorption of dilute $\text{PFOS}_{(\text{aq})}$ and $\text{PFOA}_{(\text{aq})}$ to acoustically cavitating bubble interfaces was greater than equilibrium expectations due to high-velocity bubble radial oscillations; 2) Relative $\text{O}_{3(\text{g})}$ oxidation kinetics of $\text{I}_{(\text{aq})}^-$ and $\text{SO}_3^{2-}/\text{S}_2\text{O}_3^{2-}$ were at variance with previously reported bulk aqueous kinetics; 3) Organics that directly chelated with the $\text{BiO}_x\text{-TiO}_2/\text{Ti}$ anode were oxidized by direct electron transfer, resulting in immediate CO_2 production but slower overall oxidation kinetics. Chemical reactions at aqueous interfaces can be the rate-limiting step of a reaction network and often display novel mechanisms and kinetics as compared to homogeneous chemistry.

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