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Organic Structure/Reactivity Relationships for Probing the Reactivity of Mineral/Water Interfaces

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Physical organic chemists have long used systematic variations in the functional groups and molecular structure of organic reactants to explore reaction mechanisms. To extend this approach towards investigating ligand-assisted dissolution of iron(III) and chromium(III) (hydr)oxides, it is useful to employ the following reaction scheme: $M(\text{surf}) + L(\text{aq}) = ML(\text{surf}) = ML(\text{aq})$. Capillary electrophoresis enables us to simultaneously monitor $L(\text{aq})$ and $ML(\text{aq})$, which in turn enables us to distinguish the adsorption step from subsequent metal atom detachment. The placement of amine Lewis Base groups is crucial. With iminodiacetate, an amine group is part of the linkage between two carboxylate groups. As a consequence, adsorption is low but overall dissolution rates are high. With aspartate, the amine group is not part of the linkage - it resides on a side arm of the molecule. As a result, adsorption is high but overall dissolution rates are low. Structure-reactivity relationships can also be used to investigate reductive dissolution reactions. Here, we are interested in how the placement of carbonyl groups relative to one another affects reactivity towards manganese(III,IV) (hydr)oxides. Extents of adsorption are low and electron transfer rates high, making it difficult to distinguish the two reaction steps. Structural changes that increase electronic delocalization (i.e. involving both carbonyl groups) give a substantial boost to overall reaction rates. For all types of surface reactions, structure/reactivity relationships provide the basis for making predictions. Knowing the functional groups and molecular structure of extracellular biochemicals (e.g. a siderophore) or synthetic organic contaminants (e.g. a herbicide) becomes the first step in evaluating reaction mechanisms, reaction timescales, and ultimate fate.