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Metastable Solids—Terra Incognita Awaiting Discovery

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Solid-state reactions are typically characterized by high temperatures (> 500 °C) and long reaction times (from several hours up to weeks). Both can be directly related to the significantly lower diffusion coefficient in the solid state ($D \approx 10^{-16}\,\mathrm{m^2\,s^{-1}}$) as compared to fluid phases ($D \approx 10^{-9}\,\mathrm{m^2\,s^{-1}}$), and illustrate the applicable difference between solid-state reactions and solution-based chemistry. The high temperatures and the long reaction times of conventional solid-state reactions are moreover accompanied by thermodynamic reaction control, and as a consequence, the formation of the thermodynamically most stable products.

The essential difference between thermodynamic and kinetic reaction control is best illustrated by a simple question: What would organic chemistry be under thermodynamic control? It would be restricted to products such as elemental carbon, water, carbon dioxide, and nitrogen. Kinetic control, in contrast, gives access to the virtuosic modification of functional groups with the molecule's scaffold remaining unaffected—a characteristic feature of the reactions and chemistry of molecules. Then, multistep reactions become possible that are rare for solid compounds because of the much higher activation energy.

How Do We Speed Up a Solid-State Reaction?

The lower the activation barrier (EA) between two solid phases in a phase system, the more challenging the synthesis of metastable solids (M; Figure 1). Like a mountaineer climbing from one safe ledge to another, a chemist has to carefully design the synthesis strategy in order to precisely reach the aimed metastable solid on the global energy landscape. High reaction temperatures instead lead to a crossing of most of the activation barriers—the mountaineer would rush into the global energy minimum (T) of the system. Since temperature-driven diffusion of atoms/ions in a solid lattice is not a viable option, the question is how do we otherwise speed up the reaction of solids at low temperature?

While solid-state chemistry in its original sense refers to an interdiffusion in the absence of any fluid phase (liquid or gas), strategies that partially include fluid phases are well known to speed up solid-state reactions in a broader sense. For instance, this includes chemical transport reactions, and hydro-/solvothermal synthesis, as well as reactions in molten salts or fused metals.

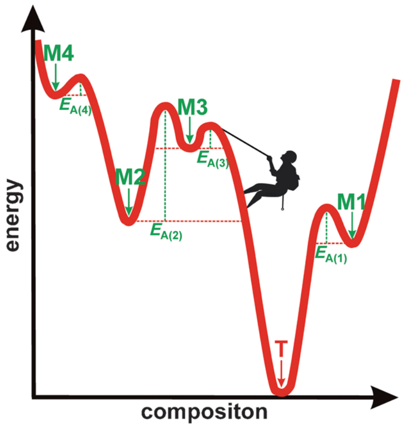

Figure 1. Energy landscape of a phase system with the global minimum (T) and local minima of metastable solid compounds (M).

Involving fluid phases, especially of solvents, is definitely the key to kinetically controlled reactions and metastable solids. Among the available fluid phases, however, nonpolar solvents often remain inert, whereas polar solvents can lead to an irreversible coordination and/or a destructive dissolution of the solid. Meanwhile, there are strategies available to modify solid compounds with an almost similar virtuosity as for molecular chemistry.

Nanoparticles

Nanoparticles as intermediates between the finite molecule and the infinite solid are obviously suited for kinetically controlled multistep reactions. Based on LaMer's model of nucleation and growth, the size and shape of nanoscale solids can currently be controlled with excellent precision. Shape, for instance, includes spheres, hollow spheres, rattles, cubes, octahedra, tetrapods, urchins, and many more forms of metastable solids. Structure and chemical composition expand these possibilities to, for example, core–shell, Janus-like, or stacked structures. Exfoliation techniques allow for targeted stacking of individual layers that were extracted from a wide choice of layered starting materials. Many nanomaterials, finally, exhibit a composition that is unknown as

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a bulk compound. Catalysis in particular currently benefits very much from novel intermetallics and alloys that are available only under kinetic control. Nanoparticles can be modified almost as virtuosically as molecules, and thus, nanoparticles can be selectively covered by multisequential shells; core–shell structures can be converted to hollow spheres by dissolution of the particle core; metal nanoparticles can be oxidized to metal oxides, followed by reaction to a metal nitride, and finally back to the primal elemental metal. Naturally, all these follow-up reactions are performed with the particle size and shape remaining intact—analogous to the carbon backbone of organic molecules. New structures and compositions of metastable solids can be also designed by assembling nanoparticles to highly periodic three-dimensional superlattices. Although still in their infancy, nanoparticles serving as “superatoms” have been already denoted as an extension of the periodic table.

Ionic Liquids

Ionic liquids offer unique options for low-temperature synthesis under quasi-gaslike conditions. The predominant features of ionic liquids are their huge volumes and the weakly coordinating properties of the constituent cations and anions. Although there is a direct relation to classical molten eutectic salts (e.g., LiCl/KCl and Na_2CO_3/K_2CO_3), reaction temperature, corrosiveness and tendency for coordination/incorporation of the salt constituents are much lower for ionic liquids. The realization of a chlathrate-like modification of germanium, unique coordination compounds and clusters, novel halogen-rich compounds, and ionothermal synthesis of metal-organic frameworks impressively show the potential of ionic liquids for preparing metastable solids. Taking the enormous electrochemical window of some ionic liquids into account, we have just caught a glimpse of the potential. In principle, even elemental cesium and fluorine can be handled in ionic liquids, and electrochemical generation of Al, Na or F_2 below 100 °C could become possible.

Gas-Phase Deposition

The required activation energy means that solid compounds typically react at high temperatures only. Although complex and time-consuming, plasma-induced co-deposition of reactive atoms on a cold substrate is an alternative access to metastable solids. Gentle warming of statistical solid mixtures of Na and N atoms, for example, results in the formation of Na_3N. Once the existence of such a metastable solid is shown, alternative routes for a more straightforward, larger-scale preparation are often found as well.

Composites and Hybrids

Composites and hybrids combine the best of two or more solid compounds. As an example, SiO_2 can show fluorescence, superparamagnetism, unpaired electron spins, or be used for pH indication or drug delivery, after embedding or adhering fluorescent dyes, iron oxide nanoparticles, radicals, pH indicators, or pharmaceuticals. Thus, various properties and functions can be combined independently from each other in one single material. Thus, real multifunctionality based on similar types of compounds and concepts of synthesis becomes possible. The precise modification of such composites and hybrids—typically comprising noncrystalline and nano- to micron-scaled solids, can be performed, again, very similar to the multistep reactions of molecules.

Computation and Prediction

As the number of metastable solids is unforeseeably high, the experimentalist would greatly profit from any reliable prediction of existing phases and their expected properties. By now, quantum-chemical thermochemistry of solids indeed affords strategies for a rational design. Thus, thermochemical data (e.g., free enthalpy) and structural models can be gained by condition-free exploration of the energy landscape. Even activation energies, vibrational frequencies, or Curie temperatures become available from ab initio methods with good accuracy. Computational exploration will clearly not supersede the experimental. The opposite is true: it is likewise the mountaineer’s benefit to know the summit’s position, especially, since there are many more mountains awaiting a first ascent than expected. Who would otherwise care about NaCl with five-fold coordination of Na^+ and Cl^-? Knowing that such a phase may exist as a metastable solid, an inventive experimentalist will surely prepare it one day.

Why Metastable Solids?

An essential question remains: Do we need a huge number of new metastable solids? For a scientist, such a consideration is like asking a mountaineer whether a nonclimbed mountain should be excluded from a first ascent. For a chemist, a new compound is like terra incognita: the synthesis is the path to take, the proof of existence corresponds to reaching the summit, and the material’s properties are the unknown landscape to survey. Scientists, however, do not operate only at their own risks: Research needs (public) funding; new compounds implicate risks such as toxicity or environmental safety.

It is up to the scientific community to demonstrate that new materials with tailored properties are essential to solving the enormous future challenges (e.g., energy, raw materials, food, water, ecological diversity). In this context, functional materials such as semiconductors for solar cells, ion conductors for high-power batteries, thermoelectrics, porous materials for gas sorption and sequestration, nanoparticles for medical imaging and therapy, luminescent materials, sensors, catalysts and photocatalysts, magnets, transparent oxide conductors, or color pigments are intensely discussed. The vast majority of these materials are metastable solids. Many more of them are waiting to be first identified—and identification is needed prior to exploring properties and function. Likewise, the first ascent of a mountain is inevitable prior to surveying the surrounding landscape.