Crystal structure priority controlling topochemical reactions

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Having a topochemical transformation reproduced is the evidence of regularity in the succession of crystal structures of the reagent and the reaction product. The symmetry of the crystal structure can lower not only as a result of topochemical recrystallization but also due to the crystal deformation. Hence, the deformational dissymmetrization can promote the topochemical process or suppress it.

If the reagent crystal has perfect cleavage, then its surface reactivity depends on its topochemical affinity with the reaction product. If the reagent cleavage is imperfect, then the surface reaction outcome is determined by crystallochemical barriers, i.e. the restrictions of positions for structural units that are imposed on those units by the lattice symmetry. In their turn, these restrictions determine "the structural preferences" of the crystallizing phase. The preferences of that kind can be characterized quantitatively by crystallochemical priorities of Fedorov groups, i.e. by relative frequencies of Fedorov groups in crystal structures. Correspondingly, there are primary and rare Fedorov groups of crystal structures. Paradoxal kinetic stability of thermodynamically unstable crystal phases is provided by their structure being of primary (i.e. most probable) type. On the other hand, forming a crystal structure of a rare (i.e. highly unlikely) type is possible only on condition of themodynamical stability of the structure because the rarity of a Fedorov group indicates a low "crystallochemical feasibility" of the corresponding structure.

If the structures of the reagent and the reaction product are meroedrically related then an external mechanical effect can facilitate the reaction or suppress it. The result is determined by the balance of crystalline phase specific volumes before the reaction and after it. The relative frequency of the space group of a structure can be used as an auxiliary criterion for evaluating the credibility of that space group. Fedorov space groups with relative frequencies fewer than 0,5% should be considered as extremely rare ones. The rarity of the Fedorov space group of a insufficiently studied structure should be considered as an incentive for more meticulous analysis of the structure. This recommendation is especially insistent for compounds being advanced as single known representatives of a Fedorov space group.

Dispersing a crystal phase induces forming a structure with a higher crystallochemical priority. Likewise, baric effect promotes forming a structure with a more probable crystallochemical type.