

Advanced Chemistry: 2019 -Thousand waste-free solid-state syntheses from 2 mmol to industrial scale and processes with 100% yield in 26 reaction types- Gerd Kaupp

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Preparative molecular and ionic solid-state reactions (gas-solid and solid-solid) have been shown to proceed rapidly, with definite completion, at decreased activation energy, and with 100% yield, wasteless and mostly specific. It has been shown at the molecular level that local melting is not required and that anisotropic far-reaching molecular migrations occur within the crystals along crystallographic channels, cleavage planes, and to voids (including amorphous solids) upon chemical reaction (pressure release). Such mechanistic knowledge is at variance with Schmidt's topochemistry hypothesis and despite hundred fold proof also with more than 1000 wasteless 100% yield reactions (directly pure solid product, without solvent requiring workup) all across chemistry in 26 reaction types. Nevertheless, top chemists still long for (local) liquids in molecular solidstate reactions and suggest heating above eutectic temperatures, or also retrogressively they "invent" LAG (liquid assisted grinding) in order to stay with their long disproved hypothesis: they obtain poor yield, incomplete reaction, require catalysts and chromatographic workup, by denying and losing the profits from the solid-state.

Unfortunately they often avoid citing the optimal performance of solids' gasification or stoichiometric co-milling of crystals strictly below the lowest eutectic temperature (including deep cooling) without local melting. The most stunning examples out of the 26 reaction types for wasteless synthesis are otherwise not available new products under temperature control. These will be stressed, and relations to packing diagrams will be discussed. Previous syntheses are improved (100%, no catalysts, no moisture, high selectivity or mostly specificity, better use of reagents (NaHCO₃ instead of NaOH, all 4 B-H bonds of NaBH₄ instead of only one, etc.). The wasteless scaling of solid-state reactions in columns and up to 20 and 100 L ball-mills, and the possibility of continuous industrial production will be presented with actual examples, the equipment discussed. This is environmentally benign, saves the environment, cost, and labor.

Solid state organic chemistry began versus 1900 with the photodimerization of solid anthracene 1 and coumarin 2 and cinnamic acids 3. Previous claims are difficult to locate. The application of X-ray analysis to organic molecular crystals has led to a huge increase in the crystal structures available to measure the distances between reaction centers, but available concentration has not led to an improvement in understanding / prediction of reactivity in the solid state.

The term topochemistry of Kohlschütter 4 describes an alkaline hydrolysis of a crystal KAl (SO₄)₂ in gel Al (OH) 3. It was copied in 1964 to signify that the molecular and atomic movements of the crystals were limited to distances $< 2.7 \text{ \AA}$ 5. The "topochemistry" of this largely redefined hypothesis with The Hype has developed. Unfortunately, this strangely redeemed statement is still considered in textbooks and articles, even if the inactivity is often the most disturbing < 4.2 explained is not explained, because the local pressure of the problem is not taken up. Thus, the emerging gas - solid and solid - solid reactions were essentially hampered to develop,

Nonetheless, many "renowned researchers" have made their careers out of the "topochemistry" hype of 1964. Therefore, a clear challenge to the hypothesis of the "topochemistry" estate. It is the application of atomic force microscopy (AFM) which is experimentally demonstrated in the photoreactions of a solid state that requires a molecular migration and a reaction site with a geometric change. Long-known exceptions to "topochemistry" were available in its infancy. Two scientific principles have been violated: the hypothesis and the statements must be substantiated and not substantiated. The only way to relieve massive local pressure is molecular migration.

This has been published since 1992 and revised. Other images can be found in the cited original publications. In addition, near field optical microscopy (SNOM) scanning rough surfaces have been developed to independently secure these facts. If the crystalline packaging does not offer a means of migration, there

will be no chemical reaction independent of the short distances of the centers, and this can be demonstrated by the lack of sliding planes, channels and voids for telecommunications.

Solid state syntheses provide delicate products that are otherwise inaccessible. Molecular solid state reactions (also ionic) require mixing / contact and lead to a more stable product. They are governed thermodynamically. Mechanochemical reactions (bonds of mechanical rupture) counter-thermodynamically. Appropriate experimentation is easy, and scaling versus industrial production has been highlighted with more than 1,000 wastes of solvents requiring treatment.