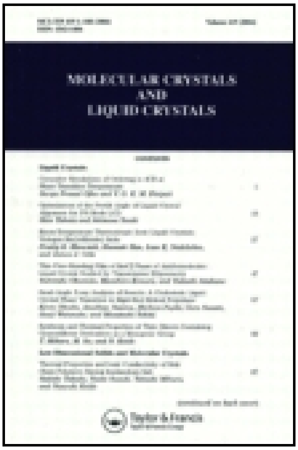

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100% Yield in 300 Gas-Solid Reactions Covering 22 Reaction Types: A Benign Option for Industrial Solid-State Production

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100% Yield in 300 Gas-Solid Reactions Covering 22 Reaction Types: A Benign Option for Industrial Solid-State Production

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Solvent-free reactions are environmentally benign, but only if they give 100% yield. If gases react with organic crystals to produce product crystals without intervening liquid phases the yield is usually quantitative, because phase rebuilding and phase transformation are followed by crystal disintegration. That sequence of events is derived from AFM, SNOM, and X-ray data via face selective surface features. Limitations and remedies are discussed. Shrinking volumes as in linear solid-state dimerizations of interlocked 1,1-diarylethenes leads to voids. Halogen additions of stilbene occur quantitatively. Tetra-*p*-bromophenylethene is also quantitatively formed. As gas-solid reactions proceed efficiently and do not usually require fine milling, they qualify for future industrial productions of almost every reaction type.

Keywords: gas-solid reactions; AFM; 1,1-diarylethylenes; stilbenes; linear dimerization; waste-free; environmentally benign

INTRODUCTION

The achievement of environmentally benign organic syntheses does not only require to avoid solvents. It is also required that the yield is quantitative. Thus, reactions that run in neat liquids or melts are not highly benign if solvent consuming workup procedures are necessary. However, solid-state reactions that use lattice effects have been shown to give frequently 100% yield of one product, if gases react directly with crystals to form new crystals of the product without intermediate liquid phase.[1] More than 300 quantitative examples have been demonstrated, and some of them were upscaled to the kg region. No wastes are formed and no workup is necessary if the starting crystals are reasonably pure. In many cases sequences of gas-solid reactions have been demonstrated.[1,2]

Table 1 gives a survey of the 22 reaction types studied so far. We have an almost complete cross-section through organic synthesis from inclusion via electron transfer to cycloadditions and even diazotations.[2] If reactants are not gaseous, solid-solid reactions can be performed in very high yield, however, these are not always fully quantitative and require continuous mixing/grinding.[3]

TABLE I Gas-solid reaction types

inclusion reactions
electron transfers
proton transfers
oxygen transfers
oxygenations
additions of RR'NH, H_2O, ROH
additions of halogens and HX
eliminations
catalyzed rearrangements
C-C bond formations
carboxylations with CO_2
condensation of carbonyls
cycloadditions
cycloreversions
substitutions with RX
aromatic substitutions
cyclizations
methylations
nitrations at N and C
diazotations
azocouplings
Sandmeyer reactions

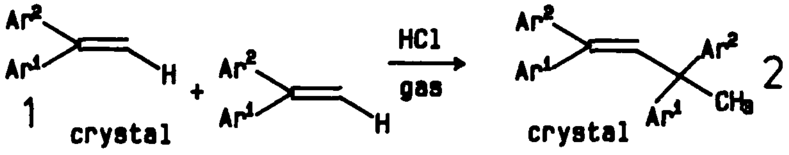
SOLID-STATE PERFORMANCE

The reasons for the good performance of gas-solid reactions have been elucidated by atomic force microscopy AFM and scanning near-field optical microscopy SNOM.[1] Thus, gas-solid reactions without liquid phase run to completion because of efficient three-step mechanisms. The first step is phase rebuilding with feature-forming long-range molecular movements that are strictly guided by the crystal packing. The second step is phase transformation when the highly rebuilt initial lattice suddenly transforms, though locally, into the product lattice. The third step is detachment of the transformed product crystals that is frequently accompanied by crystal disintegration, both with formation of fresh surface for further reaction.

While the face dependent characteristic surface feature formations are well understood in terms of crystal packing effects that guide the molecular migrations on easy ways over tens and hundreds of nm,[1,2] there are also limits to the gas-solid technique. AFM reveals if solid-state reactions are stopped by nanoliquids or surface passivation.[1,2] If movements of organic molecules are hindered in reactions which increase the volume, the reactions can only start and develop around defects according to the island mechanism that was substantiated by SNOM[1,4] and secured by X-ray grazing incidence diffraction.[5] If the volume decreases and molecules are severely interlocked, columnar or conical voids are the only choice.

LINEAR DIMERIZATION

The shrinkage mechanism is present in synthetically useful linear dimerizations of crystalline 1,1-diarylethenes **1** that give 100% **2** under the action of gaseous HCl at -50 (**a**: Ph/Ph, frozen liquid), -25 (**b**: Ph/*p*-Tol, *E*/*Z* = 33:67, frozen liquid; **c**: *p*-Tol/*p*-Tol; **d**: Ph/*p*-Anis, *E*/*Z* = 15:85) or 25°C (**e**: *p*-Tol/*p*-Anis, *E*/*Z* = 52:48; **f**: *p*-Anis/*p*-Anis). The yield of **2d** (same *E*/*Z*) is also 100% if HBr or BF_3 is the catalyst. Conversely, **2a** forms in only 50% yield in acidic organic solutions.[6] The crystal structure of **1d**[7] (Fig. 1) shows that protonation can occur via methoxy groups to the double bonds from the top face (100). The dimerization starts head to tail. It can be seen that the interlocked monomers are not able to move independently. Thus, the expected voids are formed in the AFM topography (Fig. 2).



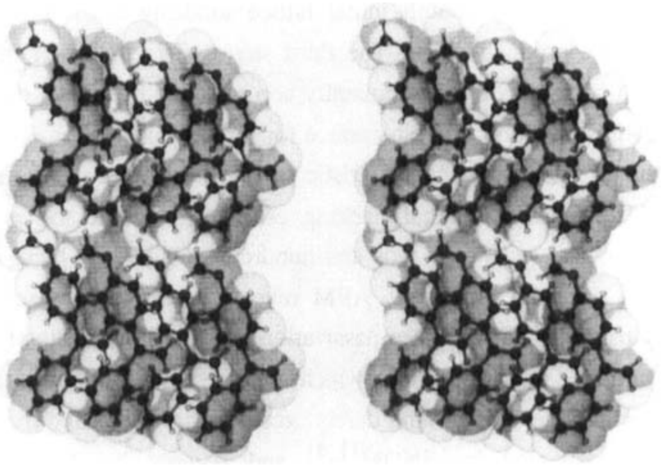


FIGURE 1 Molecular packing of **1d** (Cc) on (010), showing interlocked molecules that can accept protons and shrink when forming (*Z*)-dimer **2d**; the (100) face is seen on top. (See Color Plate II).

Starting from a closed surface with molecular terraces, not very much happens on it upon three applications of HCl gas, but huge voids form that have no walls around them and increase upon prolonged reaction. The columnar hole in Fig. 2b has a width of 8 μm and a depth of 400 nm down to a flat bottom, due to mere shrinking.

The packing in layers is responsible for the lack of oligomerization. The protons are simply transferred to the next monomer via protonation of the adjacent methoxy group. The stereoselection of **1d** favoring the (*Z*)-dimer with its vinyl-H resonance at slightly lower field (δ = 6.70) than the (*E*)-isomer (6.68) can be explained from the crystal structure. After head to tail interaction of two molecules **1d**, with the substituents on the same sides, the deprotonation to an adjacent molecule of the next layer appears geometrically easier if the bond rotation turns the larger anisyl group inwards while forming the planar double bond.

Solid **1d** and 1,1-di-*p*-chlorophenylethene (**1g**) add quantitatively chlorine gas at 20°C (3 h) giving the 1,2-dichloro-1,1-diarylethanes which eliminate HCl quantitatively at 30 - 40°C (3 h) to produce 100% yields of the two

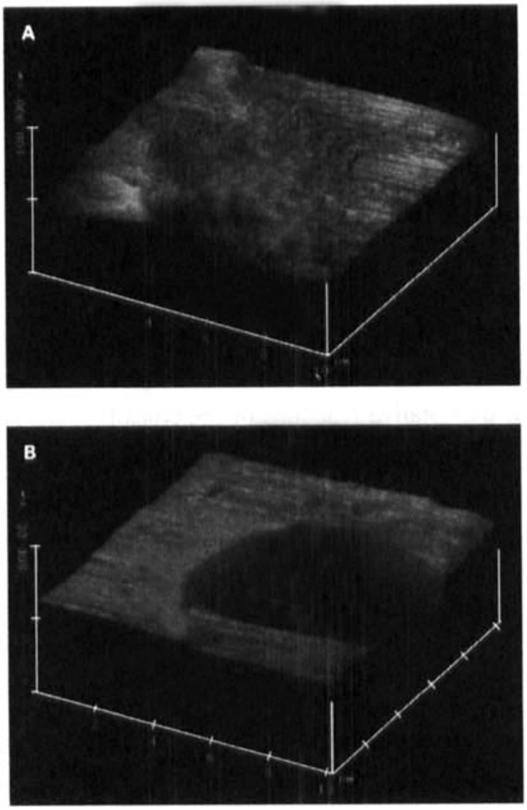


FIGURE 2 AFM topography of **1d** on (100): (A) fresh; (B) after three applications of 1 ml gaseous HCl. (See Color Plate III).

1-chloro-2,2-diarylethenes.

Similar gas-solid halogen additions to stilbenes were reported as not fully quantitative, due to difficulties with the detachment of the product crystals (step 3 of the mechanism).[8] That problem could be solved for these cases by milling of the starting crystals to < 1 μm grain size. These reactions had to be started cautiously at 0°C with 0.05 bar of Cl_2 or Br_2 to keep the reaction rate down. After 3 h, the additions are completed by leaving at r.t. under 0.5 bar of Cl_2 (3 h) or 0.1 bar of Br_2 (1 d) to give 100% of mixtures of *d,l/meso* adducts in the ratios 82:18 and 75:25, respectively. The increase in *cis*-addition is significant under these conditions, but *trans*-addition does still occur in the crystal to a large extend. Aromatic bromination in the *trans*-stilbene reaction is avoided if no excess of bromine is applied.

Tetraphenylethene does not add Br_2 to its double bond, but provides quantitative aromatic *para*-bromination giving a 100% yield of tetra-*p*-bromophenylethene, a reaction that is autocatalyzed by the HBr that forms. The lack of chlorination of tetraphenylethylene even with μm grain size material at 20°C is probably due to severe surface passivation or nanoliquids formed on the surface. The details are being studied by AFM.

The application of new mechanistic knowledge led to already more than 300 examples of quantitative reactions of the types that are given in Table 1 and described in the literature.[1,2] Our gas-solid reactions proved their power for environmentally benign syntheses also for larger scale solid-state reactions. Milling is not usually necessary to obtain a quantitative yield. Frozen liquids work as well. In cases of nonreactivity in the solid-state, the reasons can be elucidated by AFM and crystal structure determination.

References

[1] G. Kaupp, in *Comprehensive Supramolecular Chemistry*, edited by J. E. D. Davies (Elsevier, Oxford, 1996), Vol. 8, p. 381 - 423 and 21 color plates; *Chemie in unserer Zeit* 31, 129 (1997).

[2] G. Kaupp, J. Schmeyers, M. Haak, T. Marquardt, and A. Herrmann, *Mol. Cryst. Liq. Cryst.* 276, 315 (1996).

[3] K. Tanaka and F. Toda, *Chem. Rev.*, in press; G. Kaupp, M. Haak, and F. Toda, *J. Phys. Org. Chem.* 8, 545 (1995).

[4] G. Kaupp, A. Herrmann, and M. Haak, *J. Vac. Sci.*, in press; G. Kaupp, A. Herrmann, *J. Phys. Org. Chem.*, accepted.

[5] A. Herrmann, G. Kaupp, T. Geue, and U. Pietsch, *Mol. Cryst. Liq. Cryst.* 293, 261 (1997).

[6] G. Evans, N. Jones, P. M. S. Jones, and J. H. Thomas, *J. Chem. Soc.* 2757 (1956).

[7] Y. Y. Wei, B. Tinant, and J.P. Declerc, *Acta Cryst.C* 43, 86 (1987).

[8] G. Kaupp and D. Matthies, *Chem. Ber.* 120, 1897 (1987).