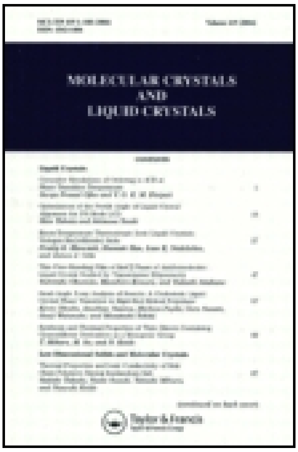


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Atomic Force Microscopy in Organic Gas/Solid Reactions: How Do the New Phases Build Up?

Gerd Kaupp [a]

[a] University of Oldenburg, FB 9 - Organische Chemie I -P.O. Box 2503, D-2900, Oldenburg, Germany

To cite this article: Gerd Kaupp (1992): Atomic Force Microscopy in Organic Gas/Solid Reactions: How Do the New Phases Build Up?, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 211:1, 1-15

To link to this article: http://dx.doi.org/10.1080/10587259208025800

Mol. Cryst. Liq. Cryst. 1992, Vol. 211, pp. 1–15
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

ATOMIC FORCE MICROSCOPY IN ORGANIC GAS/SOLID REACTIONS: HOW DO THE NEW PHASES BUILD UP?

GERD KAUPP
University of Oldenburg, FB 9 - Organische Chemie I -
P.O. Box 2503, D-2900 Oldenburg, Germany

(Received July 10, 1991)

Abstract Numerous gas/solid reactions are studied on microscopically smooth surfaces by atomic force microscopy (AFM). Five basic types for solid phase to solid phase transformations have been found, as well as mixed types. These are discussed in some detail, exemplified, and compared to some solid state photoreactions in order to provide a basis for a real understanding of non isotypical solid state transformations, which are preparatively useful.

Keywords: atomic force microscopy, gas/solid reactions, basic mechanisms, phase transformations, surface pictures, types of solid to solid reactions

INTRODUCTION

Organic gas/solid reactions from solid to solid are varied in numerous fields of chemistry.[1 - 4] In many cases they proceed quantitatively and so efficiently that there is preparative use in the production of sensitive new compounds up to the kg scale[3] without any solvent. The occurrence of such processes is still not predictable. In all cases new solid phases have to be formed and this is least understood at present. With the recent advent of atomic force microscopy (AFM)[5] a tool has become available for the study of details of the solid state to solid state transformations. We present unprecedented results which have been obtained with a commercial atomic force microscope.[6]

EXPERIMENTAL

A Nanoscope®II version 5[6] was used in its standard high voltage (220 V) configuration with head D (sensitivity XY: 333 Å/V; Z 100 Å/V; maximum range 15000 nm XY and 4000 nm Z) by using commercial silicium nitride cantilevers and tips. The spring constant was .12 N/m. All measurements were done in the height mode at optimized gain settings and force settings in the 10^{-8} N range. Planefit devices were used and median and low pass filters applied. Details have been worked out by higher enlargements of the vertical scale and also by lateral enlargements which go far beyond the possibilities of light microscopy. Flat and smooth uncoated crystals were glued to adhesive tabs on magnetic supports as horizontally as possible (<10°). Usually, the largest faces of the crystal were investigated. Microscopic inspection indicated similar changes on all other faces in most cases, and usually the reacted material of the surface could be removed after the reaction by touching it under the microscope with a needle.

Crystals were grown by sublimation in a sealed tube under vacuum (<u>1</u>; <u>5</u>; <u>10</u>) or by crystallization from solutions by slow evaporation of solvent (<u>2</u>: ethanol, rectangular plates; <u>3</u>: methanol, tiny plates <.1 mm; <u>7</u>: methanol, rectangular plates; <u>8</u>: acetone).

Gases were applied directly under the AFM by using a syringe in open atmosphere or in an empty standard liquid cell. Irradiations were performed with a Hanau 150 W Hg-high pressure lamp which was surrounded by a water-cooled Solidex mantle at a distance of 5 cm to the adjusted crystal directly on the AFM.

All chemical transformations were previously performed on a preparative scale with polycrystalline ground material, and the product structures were established by the usual spectroscopic techniques.[1-4,7]

TYPES OF SOLID TO SOLID TRANSFORMATIONS

At present, there are known at least five different basic mechanisms for the solid phase to solid phase transformations (Figure 1, A - E) and numerous mixed types, which proceed from the surface.

<u>Type A</u> is quite simple. New flat crystals emerge just

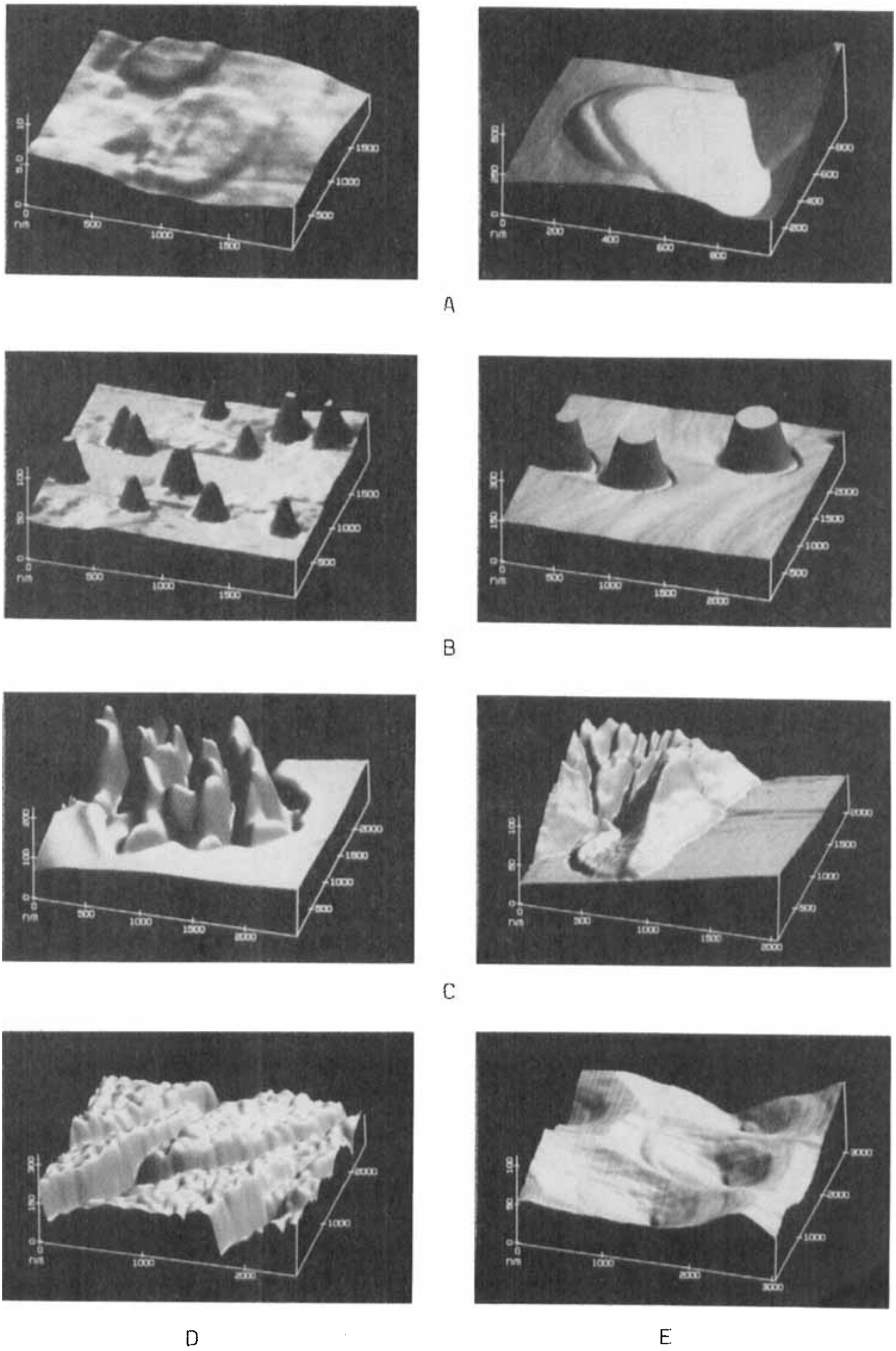


FIGURE 1 Basic types of new solid phase formations

upon the smooth surface. Apparently, there is a minimum amount of material transport involved. The right hand picture shows that such new solid phase formation may profit from specific sites like bends even though all proceeds smoothly. This mechanism appears to be not very efficient. The surface will be covered by a thin layer, which will passivate it towards further attack unless there is particular stress which provides for cracks or unless the new crystals detach themselves from their support. The new apparently crystalline layers may contain less than ten or several hundred molecular layers as in the picture A.

Type B is a process at random. New hills grow on the surface (these are more like calottes, of course, and not very steep) up to enormous heights (e. g., thousand molecular layers). The detailed pictures show that there are more or less pronounced grooves around the hills, but this is not so with all of the features in the left hand picture. Evidently, the material is pressed up from the initial crystal while it reacts with the gas which enters through the grooves if the volume increases by the reaction. It is evident from the pictures that the new material is solid. However, it cannot be told directly whether it is crystalline or amorphous. If, on the other hand, the separated hills continue to grow until they touch each other, and if they just don't merge as in Figure 2, crystallinity

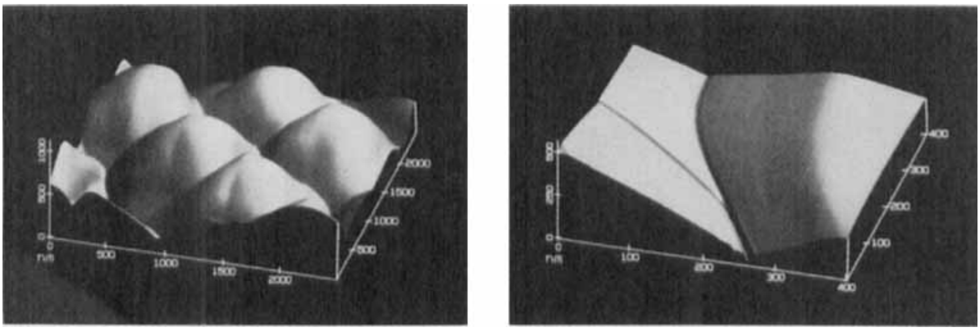


FIGURE 2 Advanced random process with vertical transport

may be assumed. Gas/solid reactions that proceed according to this mechanism may be efficient and may retain some stereospecifity as dictated by the crystal structure, even though this resembles somewhat the action of a noneruptive volcano.

Type C represents the zonal mechanism. Either a sharp or a broad front overruns the flat crystal surface. While doing that, an enormous amount of material is pressed upwards and the whole new material partly sinks down. Even though there is a groove at the sharp front, there remain numerous connections to the original material, which is reacted and fed in uphill. In the broad front case (right hand picture) the groove is less pronounced. Here the material which shows obvious signs of crystallinity must come from deeper zones of the crystal. Thus, the reactive gas must have a chance to penetrate several hundred or even thousand molecular layers down into the crystal in order to react there apparently along the proceeding groove. This mechanism is likely to proceed very efficiently with respect to the formation of cracks which will allow the crystal to react quantitatively. However, it appears that out of gas mixtures only the reactive gas (but not the unreactive gases) must be allowed to enter into the crystal. This will be most severe in the right hand case, because any unreactive gas in fissures or slits under the proceeding groove would hinder the reactive gas from penetrating to the reaction sites.

Type D is quite obvious. The reaction of the initially flat surface separates the reacted material with a minimum of transport by forming ridges between extremely steep valleys. The appearance of the new phase is crystalline and the gas/solid reaction may proceed downwards into the crystal with optimal release of any stress that may be produced by the chemical reaction. If the ridges do not grow upwards the product will have a higher density in this case.

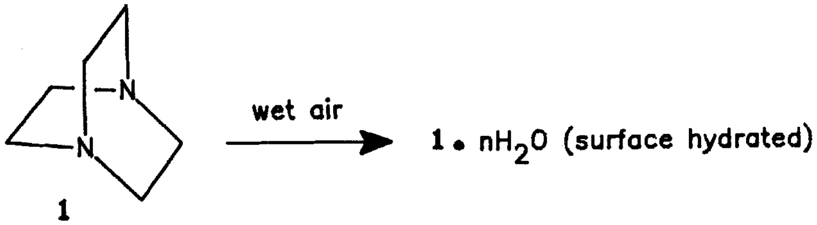
Type E is a crater type mechanism of new phase formation in gas/solid reactions. Again, this is a rather efficient solution of the transport problem. Starting from the flat surface, the reaction works itself down while building up circular rims. It appears that this mechanism provides good conditions for crystallization of the product which will have higher density than the starting crystal.

Liquid phases are absent in the types A - E above. If they occur they will be easily detected by AFM. Thus, the tip will stick to the surface if a viscid material covers the surface. This situation can be easily prepared by reacting ammonia with succinic anhydride without exclusion of moisture.[7] Liquids of lower viscosity will be spread along the scan direction by the tip on repeated scans, e. g., in the reaction of N-vinylcarbazole with methylthiol in the dark[2] at 20°C (see Figure 5). Furthermore, any distinct lines which are not in a scan direction are an indication of the solid state be it crystalline or amorphous.

EXAMPLES

There are examples for gas/solid reactions of the pure types A through E and of mixed types. Some of them will be selected and discussed here.

1,4-Diazabicyclooctane (1) is an interesting example for a flat covering mechanism. Sublimed crystals of 1 are very volatile initially, so that only large crystals (>3mm) can be studied. The first surface drawing that can be taken in air shows a complete flat covering, apparently from a hydrate. The vaporization losses come to a stop and after 1 hour the already large smooth surface covers have increased



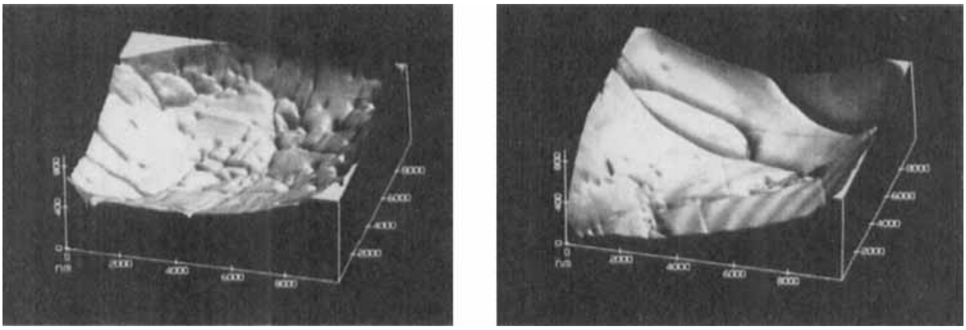


FIGURE 3 Surface covering of 1 by hydration.

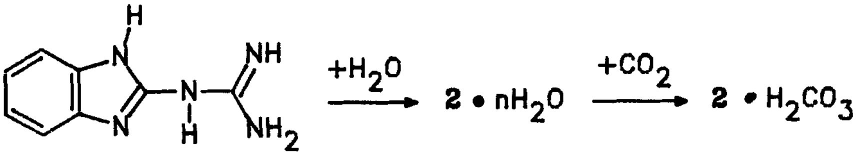
further (Figure 3). After that, the crystal does not evaporate any further but stays unchanged for days in air and does not smell intensively anymore.

It is not easy to obtain high or quantitative conversion in this type of gas/solid reaction. More frequently this is just passivation.

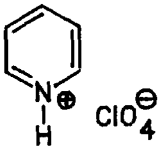
Type B occurs frequently, not only in gas/solid reactions, but also in photoreactions (e. g., irradiations of anthracene or α-trans cinnamic acid).[8] This again supports the conclusion that it is the pressure that builds up because of volume increase, which lifts the product molecules uphill.

It should be noted that impurities in carefully crystallized samples frequently show up as isolated hills similar to Figure 1 B (e. g., sublimed N-vinylphthalimide or N-vinylcarbazole[1] [see Figure 9] and recrystallized dibenzylidenecyclopentanone[8], α- and ß-trans-cinnamic acid[8] or 9,10-dibromoanthracene and further anthracenes[8]).

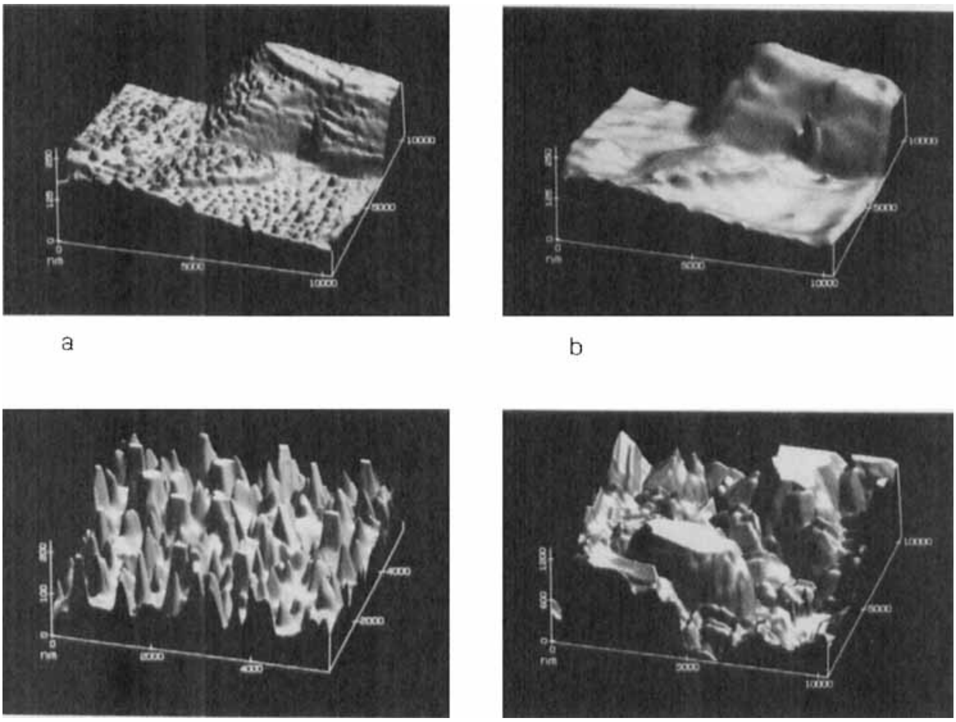
An almost pure example of type B is the hydration of the guanidine 2 (Figure 4 a), whereas its salt formation by addition of carbonic acid yields a type A flat cover mechanism (Figure 4 b). Also the hydration of pyridinium perchlorate starts with isolated hills (10 min, Figure 4 c). However, a tendency for mechanism D (ridges and steep valleys) is already discernible, and, indeed, this will continue that way (145 min, Figure 4 d).



2



3



a

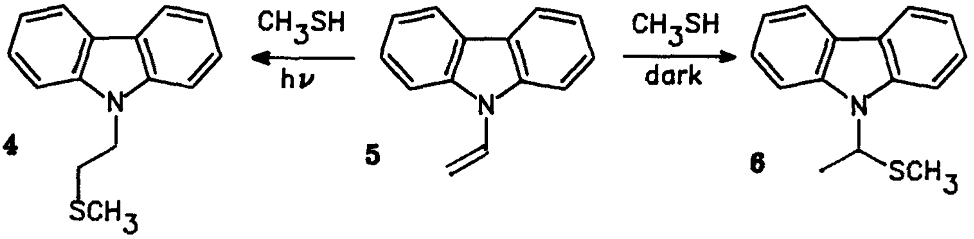
b

c

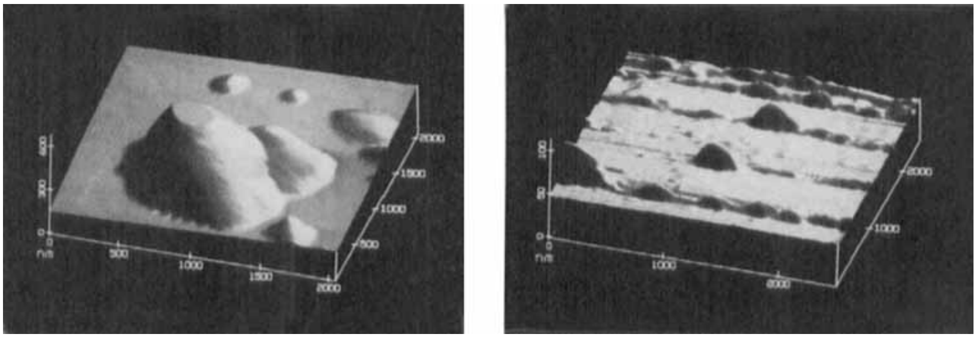
d

FIGURE 4 Hydrations of 2 (a) and 3 (c, d) and hydrocarbonate formation of 2 (b).

Also the well known gas/solid photoreaction of N-vinylcarbazole (5) with methylthiol[1,2] follows this phase transformation mechanism type B (Figure 1). It has been shown that at 0°C these are gas solid reactions which yield only



4 (photochemically) or only 6 (in the dark).[2] At room temperature these reactions are at the limit of forming liquids. Figure 5 a shows that the photochemical formation of 4 at 20°C proceeds as a random process, whereas the thermal reaction does not give a clear result, because the surface partly liquifies. Thus, if a flat region of the crystal is choosen on which some hills are present, Figure 5 b is obtained after 5 to 10 AFM scans. Thus, the tip spreads liquid material along the scan direction, and this may also be forced into new directions by changing the scan direction.

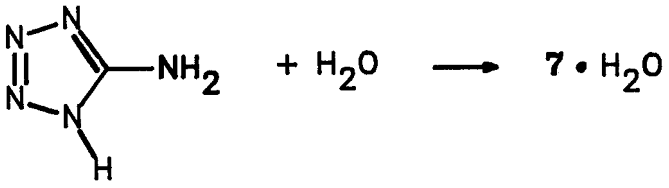


a

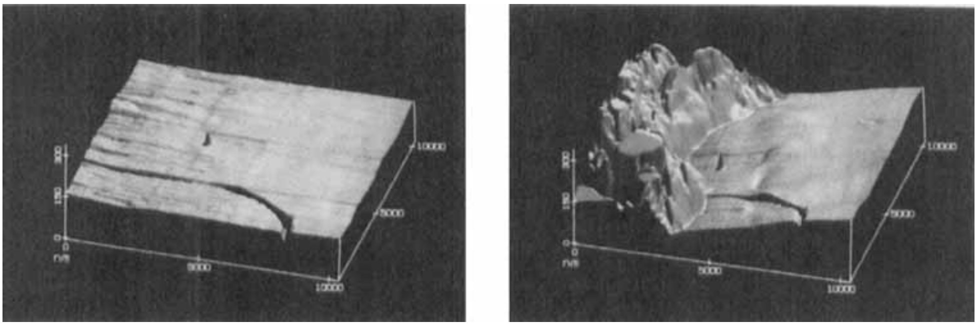
b

FIGURE 5 Photochemical (a) and thermal addition (b) of methylthiol to N-vinylcarbazole (5) at 20± 1 °C to give 4 (a) and 6 (b), respectively.

A pure type C mechanism (zonal reaction) has been observed in the hydration of 5-aminotetrazole (7). Figure 6



7

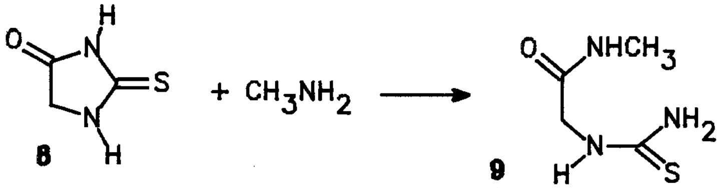


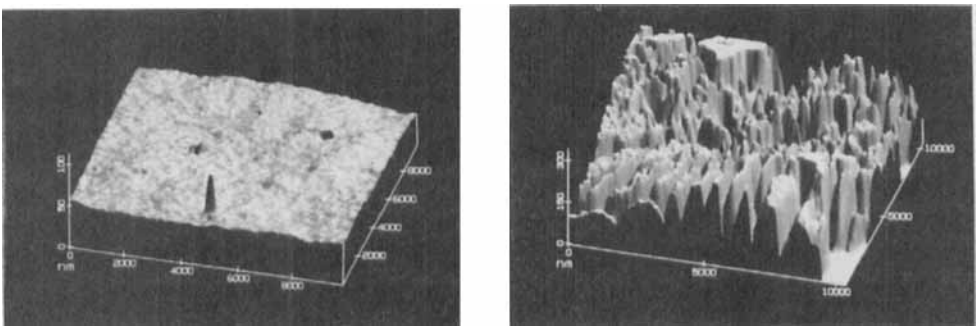
a b

FIGURE 6 Hydration of 7 before (a) and after arrival of the reacting zone in moist air

a shows the situation just before the reacting zone arrived. The stripes in the scan direction may indicate that there is a very thin liquid film on the crystal. However, this is negligible with respect to the enormous height of the reacted zone, which continued to pass this area within 10 min. After that, the whole picture looks like the situation in type D (ridges and steep valleys all over). This is already indicated in Figure 6 b (the bend of the flat part is a consequence of the planefit routine, which recalculates the whole image as flat as possible). It is remarkable that all details of the flat part in Figure 6 b are exactly the ones that were present before.

Type D situations (Figure 1) are frequently found in particular cases of mechanism B (towards the end, Figure 4 d) or C (if the ridges' formation occurs during the zonal progression). In the case of thiohydantoine (8) and methylamine to give regio-specifically 9[7] there is a random formation of ridges and steep valleys. This is shown in Figure 7. Even though the ridges are very high, the material transport is small and largely lateral rather than vertical. It should be noted that Figure 7 b indicates some tendency for crater-like structures. However, these are not predominant here.

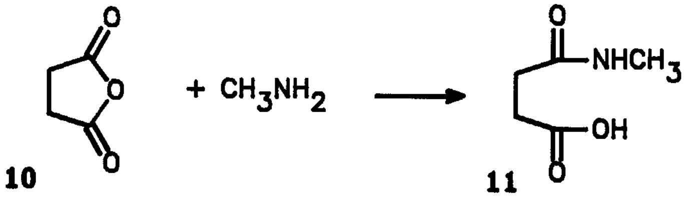


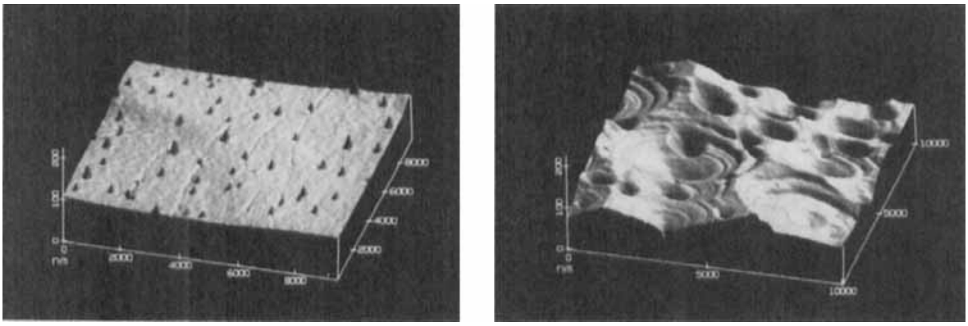


a b

FIGURE 7 Gas/solid reaction of 8 with methylamine before (a) and after application of the gas (b).

Crystal surfaces look very exciting after gas/solid reactions according to type E (crater formation, Figure 1). A striking example is the reaction of succinic anhydride (10) with methylamine to give 11.[7]





a b

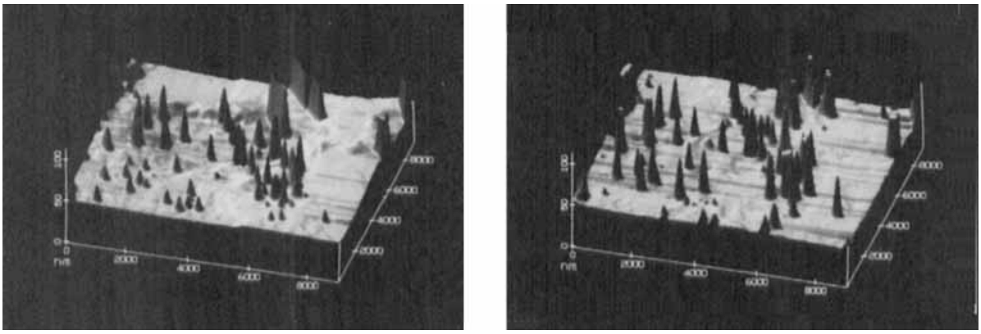
FIGURE 8 Gas/solid reaction of 10 with methylamine.

The impurities on the starting material disappear during the reaction. Even though there are grooves in the original crystal the material transport is largely lateral while deep craters are formed at random all over the surface: There are large differences in the diameters of the craters. The solid product appears to be crystalline.

CONCLUSIONS

AFM is just at the beginning in the elucidation of solid phase to solid phase transformations. It is obvious that numerous phenomena have been observed for the first time and that we hope to extend our classifications (basic types A - E) if further types emerge. The presented data should be a useful basis for the theoretical treatment of these and related solid state phenomena which could not hitherto be adequately treated. In most cases there will be a combination of more than one of the basic mechanisms, and there may be even a change in mechanism while the reaction proceeds (see Figure 4).

The mechanistic features that are outlined here apply equally to photochemical solid state reactions (without gas). Therefore, we have to show here that the mechanistic conclusion, with respect to the differences in thermal and photochemical additions of methylthiol to N-vinylcarbazole (5) is not disturbed by any photolysis of the initial surface. If 5 is irradiated in air for 10 min at a region where there are some impurities on it (these are much smaller and different from the product in Figure 5 a) it can be shown that virtually no change occurs (Figure 9).



a b

FIGURE 9 Irradiation of sublimed N-vinylcarbazole (5) in air for 0 (a) and 10 min (b) at a distance of 5 cm to a watercooled high pressure mercury lamp.

Thus, there are no particular thermal effects and no photochemical transformations of the starting material. Rather the anti-Markovnikov addition derives from a radical chain mechanism on the surface, as had been concluded earlier.[1,2]

Apart from being the sole method for this type of investigation, AFM has the advantage of being only moderately expensive and allowing for continuous scans of solid phase reactions, a fact that is of particular importance if mixed phase-transformation types occur. A disadvantage is the lack of temperature control devices which will work at such high lateral resolutions. Furthermore, one has to take into account that flat horizontal surfaces are needed, the maximum vertical movement being 4 µ with head D of the Nanoscope II. As these surfaces have to be mounted horizontally (not worse than about 10°), one encounters problems if the smaller faces of a crystal should be investigated. But usually, the most important faces of the crystals will be studied anyway. However, in some cases the study of additional faces provides further information, particularly in phototransformations.[8]

The unprecedented data show that significant material transport occurs in gas/solid reactions (and also in most solid state photoreactions). Therefore, the amount of stereoselectivity may not be extremely high and sometimes even lower than in solution.[1-3] A more detailed theoretical understanding will have to take into account the features of Figure 1 and further mechanisms that may emerge. All of this is badly needed in order to improve the predictability of solid state reactivity.

ACKNOWLEDGEMENTS

This work has been supported by a grant of the Bundesminister für Forschung und Technologie (Project Nr.01 VQ 90271) and by Schering AG, Berlin. Thanks are due to Professor Dr. W. Rammensee, Universität Köln, for his guidance in running the Nanoscope.

REFERENCES

1. G. Kaupp and D. Matthies, Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt. 161, 119 (1988); Chem. Ber. 120, 1897 (1987); 119, 2387 (1986).
2. G. Kaupp, D. Lübben, and O. Sauerland, Phosphorus, Sulfur, and Silicon 53, 109 (1990).
3. G. Kaupp, D. Matthies, C. de Vrese, Chem.-Ztg. 113, 216 (1989); G. Kaupp, A. Ulrich, and G. Sauer, ibid. (1991, in press).
4. G. Kaupp and C. Seep, Angew. Chem. Int. Engl. 27, 1511 (1988).
5. G. Binning, C. F. Quate, and C. Gerber, 1986.
6. Digital Instruments, Inc., Santa Barbara, California 93117.
7. J. Schmeyers, Diplomarbeit, Universität Oldenburg, 1991.
8. G. Kaupp, lectures at the photochemistry symposium in Waldbärenburg near Dresden (March 20 - 22, 1991) and at the XVth International Conference on Photochemistry in Paris (July 28 - August 2, 1991).