Atomic Force Microscopy of Photochemistry of 4,4'-Dimethylbenzophenone in the Solid State

Qingdao Zeng, Chen Wang, and Chunli Bai*
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P.R. China

(Received July 26, 1999; CL-990658)

The formation of regular nanostructures by photodimerization of 4,4'-dimethylbenzophenone (**1**) through intermolecular hydrogen abstraction, is investigated using atomic force microscopy (AFM) and known crystal packing data. AFM reveals that the crystal face (001) of **1** exhibits volcanoes. All the experimental results are correlated with the crystal structure. Molecular interpretation of the AFM features of **1** is given.

Atomic force microscopy (AFM) is a versatile tool. Recently, it has been applied to the submicroscopic investigation of chemical reactions on crystal solid.[1,2] These studies have revealed new perspectives in the realm of gas-solid reactions,[3-7] solid-solid reactions,[8-10] and of crystal photolyses.[11-17] AFM measurements on single crystal surfaces reveal phase rebuildings with well-directed long-range molecular transports. This was unforeseen and could only be investigated by AFM. The phenomenological description of the phase rebuilding during chemical reaction in the solid state is correlated with known crystal packing data.

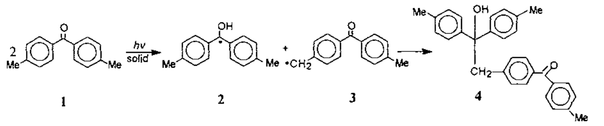
Presently, there are eight basic phase transformation mechanisms for nanostructure formation on solid surfaces.[1-3,16] Kaupp *et al.* have studied dimerization of some mono-olefin or diolefin derivative crystals using AFM and known crystal packing data.[11-17] It is of particular interest to extend these studies to photochemical intermolecular hydrogen abstraction by ketone in the solid state. In this article we present our first AFM mechanistic observation of regular nanostructures generated by photodimerization of 4,4'-dimethylbenzophenone (**1**). Molecular interpretation of the AFM features of **1** is given.

A Digital Instruments NanoScopeIII was used with commercial standard silicon nitride cantilevers and tips. The spring constant was 0.12 N/m. The forces were set at 10-30 nN throughout in constant height mode in ambient atmosphere. Flat and smooth crystal of **1** was glued to adhesive tab on the AFM support as horizontally as possible with the desired crystallographic face on top. The experiment at room temperature and in the ambient atmosphere was performed by removing the whole support with the sample immediately after the initial measurement and placing it under a high pressure mercury lamp, which was irradiated for a given time. Thereafter the support was again mounted on the AFM and measurements were done as closely as possible to the original site as judged with a microscope viewing the unchanged shape of the crystal. The AFM scans were repeated at various time intervals. 10 μ scans were usually recorded at 1.0 Hz. The experiment was reproduced at least thrice. In all cases AFM measurements were extended to other sites of the same face in order to prove uniformity of the feature.

Crystal packing drawing was generated from published X-ray crystal structure data using Cambridge Structural Database System (Laboratory of Computer Chemistry, Chinese Academy of Science, China).[18]

Single crystals were obtained as described[19] and irradiated on the AFM stage directly from 25 cm distance with a 400 w high pressure mercury lamp. Miller indice was determined by X-ray diffraction while using the known crystal data.

Ito *et al.* have reported that crystalline **1** undergoes dimerization through intermolecular hydrogen abstraction.[19]



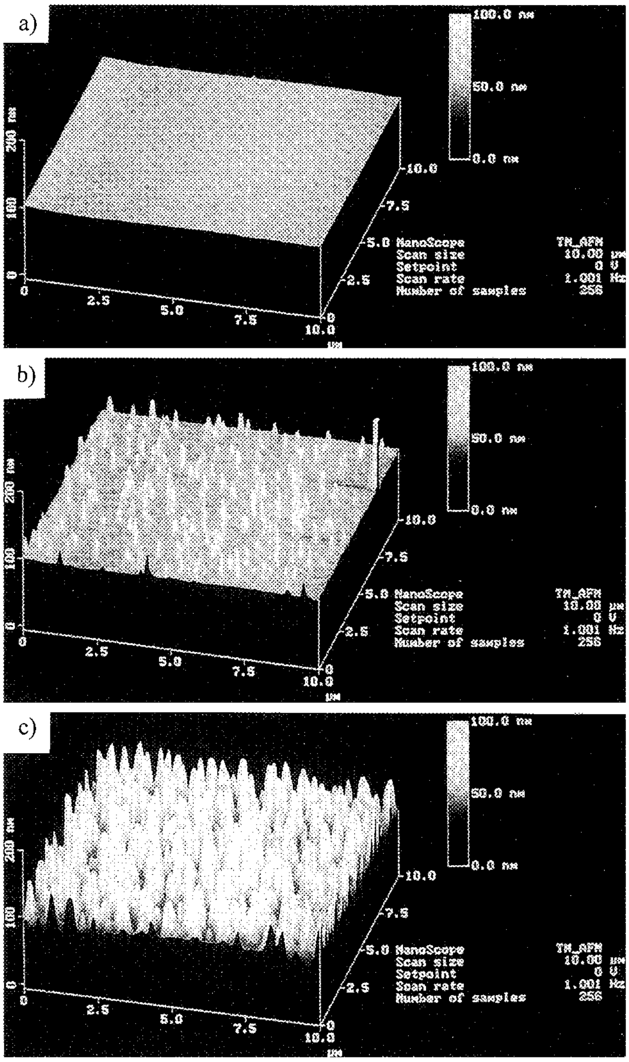


Figure 1. AFM surface of **1** on its main face (001): a) Fresh. b) After 40 min irradiation. c) After 90 min irradiation.

Figure 1 shows clearly the features of the main crystal face (001) of **1**. After 40 min irradiation the volcanoes are formed on the initially smoother (001) face ($R_{\rm ms}$ = 1.182 nm) (Figure 1a). They are about 310-395 nm wide and 20-40 nm high (Figure 1b). Upon continued stepwise irradiation, both width and height of volcanoes increase. For instance, after 90 min irradiation volcanoes are about 400-700 nm wide and 25-73 nm high (Figure 1c). The nanostructure formed seems to indicate that the phase transformation has taken place in the photodimerization of **1**. The phenomenon appears to correlate with the crystal structure of **1**.

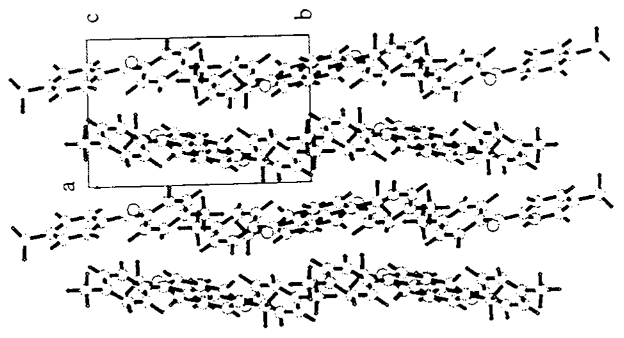


Figure 2. Stereoscopic view of the molecular packing in the crystal of **1** on (001).

In Figure 2 is given the stereoscopic view of the molecular packing of **1** on (001). It can be easily seen from Figure 2 that the molecular planes of **1** stand steeply on (001). After the reaction, the intermediate radicals **2** and **3** are produced in the crystal, and thus the original crystal lattice will become extremely distorted. Moreover, the coupling molecules **4**, once formed, can not fit in with the the original lattice of **1** because of the volume increase. They must therefore try to relieve stress by lifting themselves uphill. Due to this movement the coupling reaction can continue. Thus, the (001) surface gives rise to volcanoes, which were seen experimentally by AFM (Figure 1).

AFM provides new answers for elucidation of organic chemical reactions of crystals. The observed AFM surfaces are correlated with known X-ray crystal structures and lead to an improved interpretation of experimental results that could not be accommodated by previous methods and theories.

This work is supported by CAS and NSF of China.

References and Notes

1 G. Kaupp, *Adv. Photochem.*, **19**, 119 (1995).
2 G. Kaupp, in "Comprehensive Supramolecular Chemistry," ed by J. E. D. Davies, Elsevier, Oxford (1996), Vol. 8, p. 381.
3 G. Kaupp, *Mol. Cryst. Liq. Cryst.*, **211**, 1 (1992).
4 G. Kaupp and J. Schmeyers, *Angew. Chem., Int. Ed. Engl.*, **32**, 1587 (1993).
5 G. Kaupp, U. Pogodda, and J. Schmeyers, *Chem. Ber.*, **127**, 2249 (1994).
6 G. Kaupp, *J. Vac. Sci. Technol. B*, **12**, 1952 (1994).
7 G. Kaupp and J. Schmeyers, *J. Org. Chem.*, **60**, 5494 (1995).
8 G. Kaupp, M. Haak, and F. Toda, *J. phys. Org. Chem.*, **8**, 545 (1995).
9 G. Kaupp, J. Schmeyers, F. Toda, H. Takumi, and H. Koshima, *J. phys. Org. Chem.*, **9**, 795 (1996).
10 J. Schmeyers, F. Toda, J. Boy, and G. Kaupp, *J. Chem. Soc., Perkin Trans.*, **2**, 989 (1998).
11 G. Kaupp, *Angew. Chem., Int. Ed. Engl.*, **31**, 592 (1992).
12 G. Kaupp, *Angew. Chem., Int. Ed. Engl.*, **31**, 595 (1992).
13 G. Kaupp, *Mol. Cryst. Liq. Cryst.*, **252**, 259 (1994).
14 G. Kaupp, *J. Microsc.*, **174**, 15 (1994).
15 G. Kaupp and M. Plagmann, *Photochem. Photobiol. A: Chem.*, **80**, 399 (1994).
16 G. Kaupp, *Mol. Cryst. Liq. Cryst.*, **242**, 153 (1994).
17 G. Kaupp and M. Haak, *Angew. Chem., Int. Ed. Engl.*, **35**, 2774 (1996).
18 F. H. Allen and O. Kennard, *Chemical Design Automation News*, **8**, 131 (1993).
19 Y. Ito, T. Matsuura, K. Tabata, M. Jiben, K. Fukuyama, M. Sasaki, and S. Okada, *Tetrahedron*, **43**, 1307 (1987).