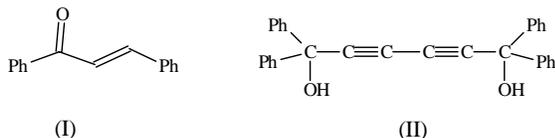


HOMOGENEOUS PHOTOCHEMICAL REACTIONS IN SOLID INCLUSION COMPOUNDS

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In heterogeneous topochemical reactions, at certain extent of conversion, phase separation occurs. In contrast, homogeneous topochemical reactions are characterized by the persistence of the crystal throughout the whole conversion range. In a specific example it was shown that when the wavelength of the absorption maximum was used, heterogeneous reaction took place. However, a single-crystal-to-single-crystal photodimerization was observed when the wavelength of the flank of the absorption was chosen (1). The method is currently being used for the study of the effects of photodimerization of guest molecules on neighboring host molecules. Benzylideneacetophenone (I) undergoes solid-state photodimerization under irradiation of its inclusion compound with 1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol (II). The guest molecules are linked to the host by hydrogen bonds. Two guest molecules are related by inversion center, therefore the dimer adopts the syn head-to-tail configuration. λ_{max} of the absorption spectrum is 244 nm and irradiation at this wavelength is heterogeneous and causes crystal destruction. Irradiation of the crystal at the absorption tail (480 nm) is homogeneous and the crystal persists at the range of the conversion reached. Crystal structure elucidation after irradiation shows that at 5% conversion the photodimerization takes place with no effect on the structure of the host molecule, suggesting that the space occupied by the guest molecule is sufficient for the production of the dimer.

(1) Novak, K., Enkelmann, V., Wegner, G. and Wagener, K.B., Angew. Chem. Int. Ed. Engl. 1993, 32, 1614.



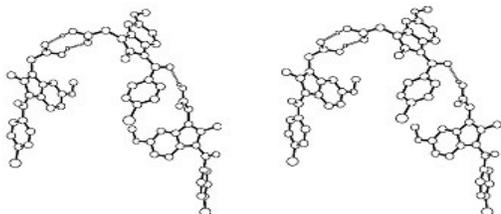
Keywords: PHOTOCHEMISTRY SOLID-STATE REACTION INCLUSION COMPOUNDS

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REACTIVITY DIFFERENCES OF INDOMETHACIN SOLID FORMS WITH AMMONIA GAS

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The reaction of ammonia gas with various solid-state forms of indomethacin, a non-steroidal anti-inflammatory drug, has been investigated. Two anhydrous crystalline forms (α - and γ -indomethacin) and amorphous material (prepared from the melt) were studied to investigate the relationship between structure and reactivity in the solid state. The ammonium salt products were analyzed by X-ray powder diffraction, gravimetry (Nessler's reagent), spectrophotometric methods, and optical microscopy, all of which confirmed the solid-state formation of the ammonium salt of indomethacin. The crystal structure of the metastable α -indomethacin was determined using X-ray diffraction methods. The crystal of α -indomethacin is monoclinic in space group $P2_1$ (No. 4) with $Z = 6$, $V = 2501.8 \text{ \AA}^3$, $D_c = 1.42 \text{ g}\cdot\text{cm}^{-3}$. There are three molecules of indomethacin in the asymmetric unit with two molecules forming a mutually hydrogen-bonded carboxylic acid dimer while the carboxylic acid of the third molecule is hydrogen bonded to one of the amide carbonyls of the dimer. γ -Indomethacin exists as dimers in which the carboxylic acid groups are caged by indomethacin molecules and are thus inert to reactions with gaseous ammonia. The carboxylic acid groups of α -Indomethacin, on the other hand, are freely accessible to gaseous ammonia and do react to form a crystalline ammonium salt. Moreover, the reaction of α -indomethacin with ammonia gas is anisotropic. The amorphous indomethacin reacts with gaseous ammonia to form an amorphous salt. Once formed, the ammonium salts metathesis back to ammonia gas and indomethacin.



Keywords:
POLYMORPH,
AMORPHOUS,
SOLID-STATE
REACTION

THERMAL SOLID-STATE ISOMERIZATION REACTIONS IN Re AND Mo 'PIANO STOOL' ORGANOMETALLIC COMPLEXES

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Piano stool complexes of the type $(\text{MeCp})\text{M}(\text{CO})_n(\text{PR}_3)_m$ undergo thermal *cis-trans* (lat-diag) isomerization reactions in the solid state. The reactions proceed differently depending on the nature of the metal, the phosphorous ligand, and the coordinated halide group, X. In $(\text{MeCp})\text{Re}(\text{CO})[\text{P}(\text{O}^i\text{Pr})_2]\text{Br}_2$ the reaction proceeds irreversibly in the solid state from the *trans* to the *cis* isomer, and it was possible to monitor this single-to-single crystal process by determining the crystal structure at several intermediate stages of the reaction at 150°C [1]. Further single crystal analyses of the reaction at three different temperatures were carried out (in conjunction with optical microscopy, NMR, IR and DSC experiments) from which we could calculate a value of 106kJ/mol for the *trans-cis* activation energy. The molybdenum complexes, $(\text{MeCp})\text{Mo}(\text{CO})_n(\text{PR}_3)_m$, with $\text{R}=(\text{O}^i\text{Pr})$ or (Ph) also isomerise in the solid state but the reactions are reversible and do not go to completion. Powder XRD, DSC and NMR experiments were used to estimate the energies of activation for the Mo complexes, which appear to have a different mechanism that proceeds via polymorphs of mixed or pure isomers. [1] RS Bogadi, DC. Levendis, NJ. Coville, JACS 124(6), p1104-1110. [2] OG Adeyemi, L Cheng, UB Eke, DC Levendis and NJ Coville. (2002) Comptes Rendus (submitted).

Keywords: ISOMERIZATION, SOLID-STATE, ORGANOMETALLIC

NON-MONOTONOUS RELAXATION PROCESSES IN HYDROGENATED Pd-Mo ALLOYS

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We have found recently [1-2] structural characteristics of the Pd-Mo alloys changing non-monotonously during 250 hours after hydrogenation. The goal of the present work is to investigate structural relaxation peculiarities in a longer period of time and to find out the nature of this phenomenon. Using X-rays diffraction method, we found some co-existing compression phases to be created in Pd-Mo alloys after hydrogenation. Dependence on the evolution time of the number of these phases, their composition and their volume is aperiodic (including the last stages, total time of the phenomena observed is over 18,5 thousand hours). High vacancy concentration (1-2%) is found to exist in the hydrogenated Pd-Mo alloys. This concentration in the matrix remains the same for over 18 thousand hours. These vacancies are able to form small Vacancy-Hydrogen clusters (these clusters change lattice parameter in isotropic way) and they are the part of even larger (of approximately 1nm size) hydrogen-defect-metal (H-D-M) complexes (these complexes cause the elastic compression which is anisotropic). Hydrogen leaves the matrix in 100 hours (very quickly), if the complexes do not bind it. The correlation between changes of the period lattice and the elastic compression of some phase is observed. This correlation is caused directly by the self-organization processes of defect- structural states; it is probably the cause of non-monotonous character of the structural changes dependence on time.

Keywords: NON-MONOTONOUS RELAXATION, HYDROGEN, VACANCY