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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. Benzylidenacetophenone (I) undergoes solid-state photodimerization under irradiation of it's 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. λmax 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.

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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 P21 (No. 4) with Z = 6, V = 2501.8 Å3, Dc = 1.42 g/cm3. 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 carboxyls 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 γ-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 metaethesis back to ammonia gas and indomethacin.

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

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Piano stool complexes of the type (MeCp)M(CO)x(PR3)Xm 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 (MeCp)Re(CO)(P(OPh)3)Br2, 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, (MeCp)Mo(CO)5(PR3)X, with R=(O i 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).

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