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Supramolecular selectivity in solid phase catalytic hydrogenation of phenylalkynyl and azobenzene derivatives

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Abstract

Solid phase catalytic hydrogenation of phenylalkynyl and of azobenzene derivatives was studied with accordance to a mechanism proposing a supramolecular selective hydrogenation of assemblies of the unsaturated substrates on a metallic catalyst matrix.

The kinetics of the solid phase reaction is shown to be affected by a combination of three factors: intermolecular distances, intact of alignment of molecules and the rigidity of the molecular stacks.

A stepwise stereospecific hydrogenation of diphenylacetylene (DPA) via the *cis*-isomer intermediate was found, while a one-step hydrogenation to saturated bibenzyl derivative took place in the case of diphenylethynylbenzene (PEB).

Solid phase hydrogenation of azobenzene derivatives resulted in a fast reaction giving aniline derivatives as the final product.

The hydrogenation kinetics of substituted azobenzene with hydroxy- or amino-group could be significantly increased as a result of better alignment, or drastically decreased due to the increase in the rigidity of the molecular assembly.

A secondary small hydrogen–deuterium isotopic effect $k_h/k_d = 1.45$ was measured, indicating a weakening of the carbon–hydrogen bond as the rate determining step of the reacting molecule.

The presence of traces of impurities such as water or peroxides, during the process of the construction of the molecular stacks on the metallic catalyst, results in a major reduction of the hydrogenation rate as an outcome of interference in the self-assembly process.

Keywords: Phenylalkynyl; Azobenzene; Supramolecules; Hydrogenation

1. Introduction

In a previous work [1] a plausible mechanism based on π–π interactions in organized stacks of phenylacetylene derivatives on the metallic catalyst was suggested, in order to explain the catalytic nature of the solid phase hydrogenation in the absence of a solvent.

Application of such a reaction for trapping hydrogen, which evolved from electrochemical, corrosion or irradiation processes, was recently described in the patent [2].

The mechanism for the catalytic reaction was based on the well-known π–π interaction between phenylacetylene molecules [3] that involves aggregation and formation of self assembled stacks.

Mobility of the catalyst and the organic reactants is severely restricted in the solid-state and the formation of a catalyst–substrate-activated intermediate is unlikely, unless it is prearranged.

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Various reactions in solid phase, involving rigid molecular conformation were shown to be highly chemoselective [4].

The intermolecular distance in a π-stack of phenylacetylene derivative was calculated recently to be 0.35 nm [5] and a solid-state polymerization reaction in a crystal of diacetylenes, was found to occur in a crystal lattice, with a distances of less then 0.4 nm between the reacting molecules [6]. Such small distance probably enables the migration of hydrogen atoms among the prearranged phenylacetylene units inside the stacks [1].

The terms of supramolecular chemistry are very useful in explaining the reaction mechanism: as a result of π–π interaction, the phenylacetylene undergoes a self-construction process resulting in organized molecular stacks. These stacks are also coupled with the metallic catalytic sites as an outcome of a molecular recognition process. The accessibility of the metallic catalyst to the stacks enables the catalytic reaction in solid phase even in the absence of molecular mobility.

Azobenzene derivatives are also known to have intermolecular π–π interaction [7], and it will be shown here that azobenzene derivatives also exhibit a significant reactivity toward the catalyzed hydrogenation in solid phase similar to that observed in phenylacetylene [1].

The mechanism of solid alkyne hydrogenation [1] includes an initial formation of a reactive hydrogen species on the Pd catalyst, followed by an H-transfer step, which took place in the solid organic substrate.

Since hydrogen mobility inside the organized stacks may affect the reaction kinetics, various aspects, which may change hydrogen mobility, were studied by using reaction kinetic measurements and spectroscopic techniques including XRD and NMR.

This paper shed more light on both the microscopic and the macroscopic aspects of the hydrogenation mechanism of phenylacetylene and azobenzene derivatives.

2. Experimental

2.1. Methods and materials

Commercially available diphenylacetylene (DPA) and azobenzene derivatives were used following recrystallization from methanol or methanol–water.

4,4′-Diaminoazobenzene (DAAB) was prepared via coupling reaction of *p*-aminoacetanilide followed by acidic hydrolysis [8].

Commercially available supported Pd catalysts were used without pre-activation.

Activated unsaturated catalyst–substrate samples were prepared by a reduced pressure rotary evaporation of the substrate's THF solution in the presence of the powdered supported palladium catalyst. Freshly distillated and dried THF was used for the preparation of the substrate solutions.

Determination of hydrogenation kinetics was performed on a computerized standard volumetric system. In all cases, a bowl ended Pyrex tube containing about 150 mg of the solid substance was connected to the vacuum system via a glass-metal fitting flange. The hydrogenation reaction kinetics was calculated from the pressure drop, in a calibrated volume, measured with a sensitive pressure transducer (MKS Baratron model 122), calibrated to accuracy and resolution of ±0.1 Torr[2].

Hydrogenation was performed at ambient temperature in several successive stages.

The pressure of hydrogen introduced at the beginning of each stage was usually 10% of the total hydrogen capacity of the sample. Rate of hydrogen pressure decrease was recorded during the reaction and an additional hydrogen portion was added when, e.g. 98% of the gas was consumed.

Hydrogenation products were identified and analyzed by GCMS and HPLC by comparison to commercially available standards.

GCMS analyses were performed on an HP5890 GC with an HP5971A MS detector.

3. Results and discussion

3.1. Effect of impurities on reaction rates of powdered PEB/Pd solid samples

The intrinsic reactivity of molecules in a solid phase reaction is less important than the nature of the molecular packing. This could be demonstrated

[2] 460 Torr = 101.325 kPa

experimentally by the significant dependence of the hydrogenation kinetics on the mode of preparation of the catalyst–substrate-activated powder.

Rates of hydrogenation of activated mixture of 1,4-diphenylethynylbenzene and Pd/C, which was prepared by evaporation of the THF solution, were found to be depend on the THF purity.

By using a newly opened container of THF (HPLC Grade >99.9%) a fast reacting PEB/Pd solid was obtained. However, next day's preparations exhibit a gradual deterioration in the reactivity of the produced PEB/Pd solid toward hydrogenation. Reactive PEB/Pd aggregates, which was deposited from THF, freshly distilled on a sodium-benzophenone still, reacted significantly faster compared to samples were THF was left overnight following distillation.

Since it is well known that peroxides and water are common impurities in THF and both are effectively removed by a sodium-benzophenone distillation [9], it could be concluded that such impurities affect the solid PEB/Pd aggregates formation.

This retarding effect of impurities at the self-constructing stage could be related to formation of defected molecular stacks or as interference to the catalyst–alkyne coupling. The possibility of affecting the Pd/C active sites by solvent impurities is less probable, since such retarding effect was not found in heterogeneous hydrogenation in liquid phase.

3.2. Isotopic effect in hydrogenation experiments of DPA and PEB

Reaction rates profile of DPA hydrogenation with both H_2 and D_2 (Fig. 1) indicate a maximum reaction rate following the consumption of approximately 10% of the theoretical hydrogen capacity. Rates decrease gradually behind this point.

Isotopic effect however, is constant throughout the reaction. The size of the isotopic effect is 1.45, which is close to the ratio of the vibrational energy of CH to CD bond. Such a small isotopic effect indicates that bond involving the H or D atom is far from being completely broken in the activated state in such cases a regular secondary isotopic effect of the magnitude of 1.74 or less will be found [10].

A mechanism of hydrogen atom migration inside the stack could thus be described as a cleavage of a weakened CH bond rather than consecutive processes

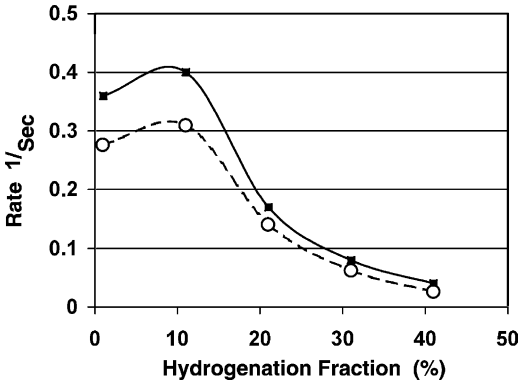

Fig. 1. Typical isotopic effect in the hydrogenation rate of DPA (filled squares) vs. deuteration rate (open circles) using five successive portions of hydrogen and deuterium. Pd:DPA molar ratio 1:24.

of dissociation and formation of CH bonds, which will result in a much higher isotopic effect.

Thus, the migration of partially dissociated hydrogen atoms between adjacent alkyne moieties in the molecular stack could explain such an isotopic effect.

NMR of PEB, which was deuterated catalytically in the solid phase, was performed following dissolution of the solid product in $CDCl_3$. Only traces of benzylic hydrogen were found at 2.89 ppm.

The integration ratio of this signal to the aromatic hydrogen show that scrambling of the hydrogen atoms, under the reaction conditions, is negligible and the aromatic hydrogen atoms are not participating in the hydrogen transfer process.

3.3. Supramolecular chemoselectivity of partial hydrogenation of phenylalkynes

NMR spectra of diphenylacetylene/Pd activated solid, saturated up to 50% of its theoretical hydrogen capacity, show that a mixture containing: bibenzyl (6%), *cis*-stilbene (32%) and unreacted DPA (62%) was obtained. The formation of both saturated and partially reduced products indicates a stepwise hydrogenation. The achieved 100% chemoselectivity toward the formation of the *cis*-isomer is in accordance with the concept of a fixed molecular conformation inside the solid phase.

It is known that lattice restrictions of intermolecular motion leads to a single product while correspond-

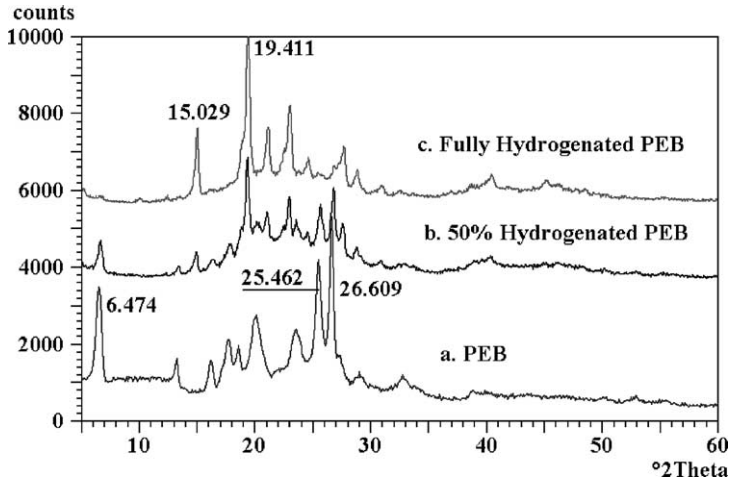

Fig. 2. Changes in XRD spectra during the hydrogenation of PEB: (a) XRD of unreacted PEB; (b) XRD following hydrogenation of 50% of calculated hydrogen capacity; (c) XRD following hydrogenation of 100% of calculated hydrogen capacity.

ing reaction in solution lead to a mixture of isomers [4]. Catalyzed hydrogenation of alkynes in solution with palladium on activated carbon is not selective to *cis*-alkene. A *cis*-selective Lindlar's catalyst [11] is being used for this purpose.

X-ray diffraction of PEB/Pd activated solid before and following hydrogenation (Fig. 2) demonstrates the changes in the crystal structure during the catalyzed solid phase hydrogenation. The diffraction pattern of partially hydrogenated sample resembles a superposition of the lines of the unreacted (Fig. 2a) and the fully hydrogenated sample(Fig. 2c).

The XRD lines of unreacted solid powder are very similar to that of crystalline pure PEB (with the addition of a broad line of the amorphous carbon). Fully hydrogenated PEB obtained by catalyzed hydrogenation in solid phase or in solution resulted in a product with identical XRD spectra (Fig. 2c).

A controlled chemoselective partial catalyzed hydrogenation of PEB in THF solution, using Lindlar's catalyst (Pd/$CaCO_3$ poisoned with lead) was stopped following 50% saturation. The alkene product of this reaction has XRD spectrum, which is completely different from that obtained following 50% saturation of the solid powder.

GCMS analysis of the PEB/Pd activated solid following partial hydrogenation indicates that there are two major components: the fully hydrogenated PEB and the unreacted one in a 1:1 molar ratio. The result is consistent with the superposition of XRD pattern obtained in partial hydrogenated PEB powder.

^{1}H NMR spectrum of $CDCl_3$ solution of this reaction mixture reveals that the integration ratio of the aromatic/aliphatic signals is 4:1, indicating a 1:1 molar ratio of the two major products.

While DPA enables a stepwise transition from sp configuration to the distorted sp^2 configuration, such a transition is forbidden in the case of PEB as a result of the need for higher distortion in the diyne stack.

These results are in accordance with the supramolecular selectivity of reactions in the solid phase, which depends mainly on the degree of freedom for conformational changes in the solid crystalline structure.

3.4. Supramolecular selectivity of hydrogenation of azobenzene derivatives

Pretreated reactive solid containing azobenzene and Pd/C (molar ratio 16:1) reacted under standard conditions with 10 successive portions of hydrogen to give the calculated amount of aniline, which was determined by GC.

Like phenylalkynes, *trans*-azobenzene undergo a catalyzed hydrogenation in the absence of a solvent giving phenylhydrazine in the first step, followed by hydrogenolysis of the hydrazine to give aniline as the final product.

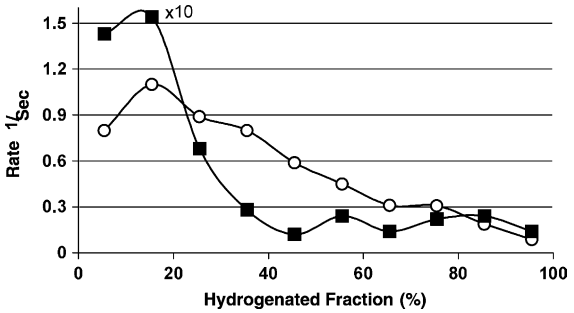

Fig. 3. Rates of hydrogenation of azobenzene (filled squares) and DPA (open circles).

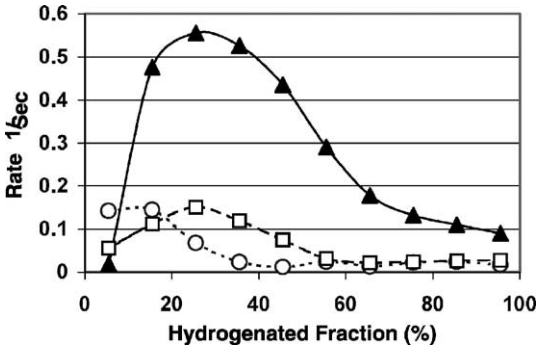

Fig. 4. Rates of hydrogenation of substituted azobenzene with 10 successive portions of hydrogen: 4-aminoazobenzene (filled triangles), 4-hydroxyazobenzene (open squares) and azobenzene (open circles).

Two distinguished kinetics were detected throughout the hydrogenation of azobenzene: during the consumption of the first five hydrogen portions (0–50% of the theoretical consumption) a fast decrease in the rate was observed, while a relative constant rate was observed for the next five H_2 portions (50–100%) (Fig. 3).

The gradual decrease in reaction rates which was observed during the hydrogenation of both azobenzene and DPA could be attributed to constrains and distortions developing in the molecular stacking as a result of the alteration of supramolecular alignment during the hydrogenation process.

The distortion occurs in the transition from the diazo to the hydrazine lattice is more significant than the one take place in the hydrogenation of the hydrazine lattice, as seen from the sharp decrease in the reaction rate (Fig. 3).

Since intermolecular hydrogen bonds formation in the newly formed hydrazine intermediate contributes to the distortion of the supramolecular assemblies, a 10-fold decrease in the hydrogenation rate is obtained.

On the other hand, the following hydrogenation of hydrazine proceeds with nearly a constant rate as a result of the stability of the assembly gained due to the newly added hydrogen bonding of the hydrazine.

In order to examine the role of H-bonding we study the hydrogenation of hydroxy- and amino-substituted azobenzene in which hydrogen bonding originally exist.

Indeed, the kinetic of the hydrogenation of 4-phenylazoaniline and 4-phenylazophenol was found to be different from the kinetics of the unsubtituted azobenzene (Fig. 4).

The faster reaction rates of 4-phenylazoaniline and 4-phenylazophenol over the rate of azobenzene hydrogenation is a result of improvement of molecular alignment in the initial assembly due both to H-bonds and appropriate intramolecular distances.

A significant increase in the reaction rate was found for the initial hydrogenation step of hydroxy- and amino-substituted azobenzenes, followed by a rate decrease.

The slowing down of the hydrogenation rate of unsubstituted azobenzene starts earlier in comparison to hydroxy- and amino-substituted azobenzenes. This could be seen from the shift to longer times of the maximum rates of the substituted azobenzene at Fig. 4 when compared to azobenzene and to DPA in Fig. 3.

The two different kinetics of NH_2- and OH-substituted azobenzene are the outcomes of the differences in the strength of H-bonds, which cause variation in molecular alignment parameters such as intermolecular distances and lattice rigidity. For a highly ordered stacks and proper intermolecular distance higher rates are anticipated, while a rigid alignment would reduce hydrogenation rate following a partial hydrogenation. This rate deceleration would result from the amplification of the lattice distortion.

The kinetics of the solid phase reaction seems therefore to be affected by the combination of intermolecular distances, intact of alignment of molecules and the rigidity of the molecular stacks.

In order to study the effect of molecular rigidity on the hydrogenation rate the kinetics of hydrogenation

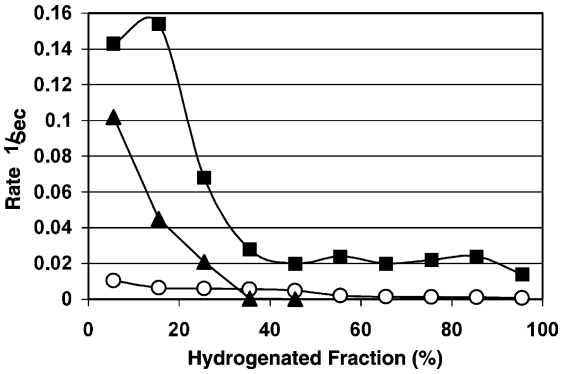

Fig. 5. Rates of hydrogenation of diaminoazobenzenes with 10 successive portions of hydrogen: azobenzene (filled squares), 2,4-diaminoazobenzene (open circles) and 4,4′-diaminoazobenzene (filled triangles).

of disubstituted 2,4- and 4,4′-diaminoazobenzene was studied as shown in Fig. 5. A lower reaction rate due to the higher rigidity of the molecular stack is observed. The poor reactivity of the diamino-derivative compared to the monoamino-derivative indicates that the driving force for these reactions is dictated by supramolecular selectivity rather than by molecular chemoselectivity. The sharp decrease in rate of 4,4′-diaminoazobenzene could be explained by the higher rigidity due to two-ends fixation of the molecules. The rate of 4,4′-diaminoazobenzene hydrogenation decreases sharply to zero at about 50% of the calculated yield, while the less rigid 2,4-diaminoazobenzene reaction proceeds to 100% saturation.

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