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Palladium-catalyzed liquid-phase hydrogenation/hydrogenolysis of disulfides

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Abstract

For the first time, the hydrogenation/hydrogenolysis of a range of disulfides has been achieved over a supported palladium catalyst using hydrogen under relatively benign conditions. These unexpected results demonstrate that it is possible to avoid the poisoning of the catalyst by either the nitrogen-containing groups or the sulfur species, allowing both efficient reaction and recycling of the catalyst under the proper conditions (e.g., at low temperatures). A slight loss in activity was found on recycling; however, the catalyst activity can be recovered using hydrogen pretreatment. The reaction mechanism for the hydrogenolysis and hydrogenation of *ortho*-, *meta*-, and *para*-dinitrodiphenyldisulfide to the corresponding aminothiophenol has been elucidated. Density functional theory calculations were used to investigate the adsorption mode of the dinitrodiphenyldisulfides; a clear dependence on adsorption geometry was found regarding whether the molecule is cleaved at the S–S bond before the reduction of the nitro group or vice versa. This study demonstrates the versatility of these catalysts for the hydrogenation/hydrogenolysis of sulfur-containing molecules, which normally are considered poisons, and will extend their use to a new family of substrates.

Keywords: Catalyst; Palladium; Hydrogenation; Hydrogenolysis; Heterogeneous; Sulfide; Nitro; Amine

1. Introduction

Thio-products, such as mercaptans, sulfides, polysulfides, sulfones, thioacids, and thioesters, have an increasing share in the industrial production of pharmaceuticals, agrochemicals, cosmetics, and petrochemical products. The synthesis of mercaptans is particularly important, because these are often used as precursors in the production of other thio-compounds. Currently, aliphatic mercaptans are produced via the direct thiolation of alcohols with H_2S over alkali metal catalysts in yields >95% [1]. In comparison, the production of aromatic thiols via this method is not efficient, resulting in low yields due to reduced selectivity at the high temperatures needed to achieve viable reaction rates [2]. Current methods for forming benzenethiol derivatives include the reduction of sulfonic acids [3] or their sulfonyl chlorides [4] with phosphorus or hydrogen, produced in situ in the presence of a mineral acid and a metal. Although these reactions are highly selective, large amounts of phosphoric acid and/or metal chloride waste are also produced.

One possible alternative route to the production of aromatic mercaptans is through reductive cleavage of the corresponding disulfides. This reaction has been extensively studied for the cleavage of S–S bonds in proteins to change their tertiary structure. This is conventionally achieved to form thiols and thiolates using stoichiometric nucleophilic reagents, such as hydrides in the form of $NaBH_4$ [5]; phosphorous compounds, such as triphenylphosphine [6]; or hydrazine derivatives, such as semicarbazide [7]. Few catalytic processes for the reduction of S–S bonds have been reported due to the potential strong chemisorption of sulfur-containing molecules and their ability to poison metal surfaces. To date, Calais et al. have reported the only process for cleaving a range of substituted diphenyldisulfides over sulfided Ni–Mo/Al_2O_3 catalyst [8,9]. The choice of cata-

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lyst was thought to be important, because it is commonly used for the gas-phase hydrotreatment and desulfurization in petroleum refining. This catalyst is able to catalyze hydrogenation and carbon-heteroatom hydrogenolysis while being highly resistant to sulfur poisoning. In this study, selective reduction of the diphenyldisulfide was achieved at 160 °C and 3 bar hydrogen [8]. After introducing *para*-substituents, such as methyl, amine, chloro, nitro and hydroxyl groups, a reduction in the rate of reaction was observed. This reduced activity was particularly evident for 4,4′-dinitrodiphenyldisulfide, where up to 200 °C and 10 bar hydrogen were required for the reaction to reduce both the nitro group and disulfide linkage to form 4-aminothiophenol. Using theoretical models, the behavior of 4-nitrodiphenyldisulfide was explained by a difference in the adsorption geometry. The molecule was thought to adsorb predominantly *via* the nitro groups, forcing the S–S bond away from the surface and reducing the likelihood of reductive cleavage. Such an effect also has been reported for other hydrogenation reactions [10]. In contrast to the reaction with hydrides, where the rate increased with decreasing aromatic electron density [5], for the catalyzed reactions, no correlation with the electronic property of the reactant was observed.

In the present study, we investigated the hydrogenation/hydrogenolysis of $-NO_2-$, $-NH_2-$, $-CH_3-$, and $-OCH_3$-substituted diphenyldisulfide as well as dibenzyldisulfide and dimethyl- and dibutyldisulfides using a carbon-supported platinum group metal (PGM) catalyst (Fig. 1). Whereas platinum and palladium are commonly used for the hydrogenation of a wide range of substrates, PGM is very susceptible to poisoning by sulfur [10–23]. This is thought to be particularly problematic on palladium; consequently, fewer studies on this have been reported. Sulfur poisoning on metals is thought to be a combination of both geometric and electronic effects, giving rise to changes in short-range and long-range interactions. The geometric effect is related to the length of the carbon chain attached to the S-atom anchored to the surface; this is, the larger the poison molecule, the larger the area of the surface blocked [11,24]. In contrast, the electronic effect results in changes in the electron density of the catalyst surface as a result of the strong covalent bonds between the metal atoms and the sulfur [19]. This is used in some cases to tune the reaction selectivity by exposing the catalyst to either dimethyldisulfide or thiophene [25,26]. For example, dimethyldisulfide is decomposed to H_2S under hydrogenation conditions at 200 °C, which then adsorbs and modifies the catalyst surface [22]. Here we report on the feasibility of using PGM catalysts for the hydrogenation/hydrogenolysis of a range of aromatic and aliphatic disulfides under mild reaction conditions.

2. Experimental

2.1. Materials

All experiments were carried out using nominal 10 wt% Pd catalyst supported on charcoal as provided by Johnson Matthey. Metal analysis of the catalyst using a Perkin–Elmer Optima 4300 ICP-OES analysis showed a Pd content of 9.93 wt%. The catalyst had a BET surface area of 1335 $m^2\,g^{-1}$ and a Pd surface area of 25 $m^2\,g^{-1}$ measured by CO chemisorption, along with a particle size of <38 μm. In all cases, the catalyst was used as received with no pretreatment. All tested disulfides were purchased from Aldrich with $>97\%$ purity. The catalyst was characterized by powder XRD before and after reaction at room temperature using a PANalytical X'PERT PRO MPD X-ray diffractometer with CuK_α radiation.

2.2. Typical reaction and recycle procedure

All reactions were carried out in a high-pressure 300-cm^3 Parr autoclave modified with baffles and a gasifying stirrer to ensure good mixing. Unless stated otherwise, 5 mmol substrate in 200 cm^3 THF was placed in the reactor with 200 mg of catalyst and heated to 75 °C under N_2 before the desired pressure of hydrogen was introduced. The speed of the stirrer rotation was

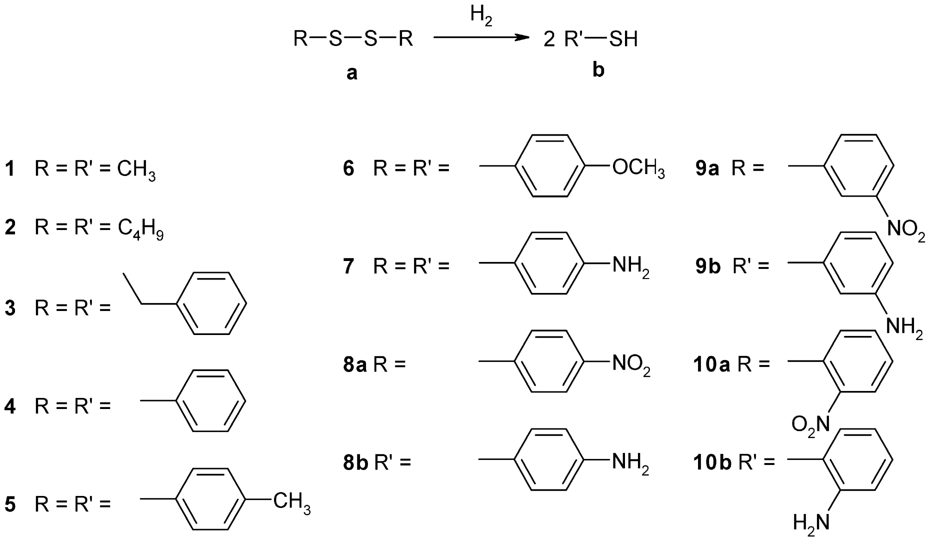

Fig. 1. Reaction scheme and notation for the disulfides used in this study.