

Liquid Phase Hydrogenation of Disulfides on Pd Catalyst

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Introduction

The industrial importance of mercaptans, sulfides and other sulfur containing molecules is continuously increasing, especially in the production of agrochemical, pharmaceutical, petrochemical and cosmetic products. At present, the majority of aliphatic mercaptans are prepared by direct thiolation of alcohols or by sulfidation of alkenes[1]. However, for aromatic thiols these methods seem to be unsuccessful and organic reducing agents, such as NaBH₄, [2] are usually employed. Unfortunately, these create additional problems with respect to product separation and waste management. Catalytic hydrogenation offers many advantages over chemical reduction. However, few catalytic processes for the reduction of S-S bonds have been reported due to their ability to poison metal surfaces.

In this study we have investigated the hydrogenation of 2-,3-,4-NO₂, NH₂, CH₃ and CH₃O substituted diphenyl disulfide ((X-PhS)₂), as well as dibenzyl disulfide ((BzS)₂), dimethyl ((MeS)₂) and dibutyl disulfide ((BuS)₂) using a carbon supported platinum group metal (PGM) catalyst. Whilst platinum and palladium are commonly used for the hydrogenation of a wide range of substrates, the PGM is very susceptible to sulfur poisoning [3]. Herein, the feasibility to hydrogenate a range of aromatic and aliphatic disulfides on a PGM catalyst and extent of the poisoning of the catalyst is reported. The kinetics and mechanism was examined with particular attention to the nitro-substituted diphenyl disulfides.

Materials and Methods

All experiments were carried out using a 10wt% Pd catalyst supported on charcoal provided by Johnson Matthey. In all cases, the catalyst was used as received without any pre-treatment. All tested disulfides were purchased from Aldrich in >97% purity. Catalytic runs were carried out in a 300cm³ Parr stainless steel autoclave operating in batch mode. In a typical run, 5 mmol substrate in 200 cm³ THF were placed in the reactor with 200 mg catalyst and heated to the reaction temperature under N₂ before introducing the desired pressure of H₂. Analysis of reaction samples was performed by GC.

Results and Discussion

The results of this work clearly show that a wide range of disulfides can be hydrogenated to thiols on Pd/C catalyst under mild reaction conditions. Furthermore, recycle of the catalyst is possible although a small decrease in reaction rate is generally observed on each recycle due to the formation of surface Pd₂S. Surprisingly, the presence of thiol, i.e. the product, is not found to inhibit the reaction. The cleavage of the S-S bond occurs selectively, independent of the hydrocarbon chain attached to the S atoms. No hydrocarbons were detected throughout the reaction. The initial rates vary with the type of the hydrocarbon chain: aliphatic or (substituted) aromatic, directly connected to the S atom or via methylene group. (Figure 1) Both aliphatic disulfides and aromatic were able to be cleaved with the highest rate found for

dimethyldisulfide. No clear trend is found with the aromatic substituent, for example the rates of the para substituted diphenyldisulfide follow the order -NH₂ > -NO₂ >> -H > -Me > -OMe.

The liquid phase hydrogenation of bis(4-nitrophenyl) disulfide to 4-aminothiophenol is of particular interest commercially. This process includes the cleavage of S-S bond as well as the reduction of the nitro group to amine. The mechanistic studies reveal complex reaction network with at least two (major) parallel routes leading to 4-aminothiophenol as the final product. Interestingly, the hydrogenation of the bis(2-nitrophenyl) disulfide to 2-aminothiophenol shows a significant change in the reaction mechanism. In the para position, cleavage of the S-S bond dominates followed by reduction of the nitro group whereas in the ortho position the reactions are reversed. DFT calculations have been used to simulate the surface process and have shown a significant change in the adsorption geometry of the starting material for the two isomers.

Significance

The hydrogenation of sulfur containing molecules over PGM catalysts, which is commonly perceived as being impractical due to sulfur poisoning, has been successfully achieved. This methodology provides an efficient method for the industrial preparation of thiol compounds.

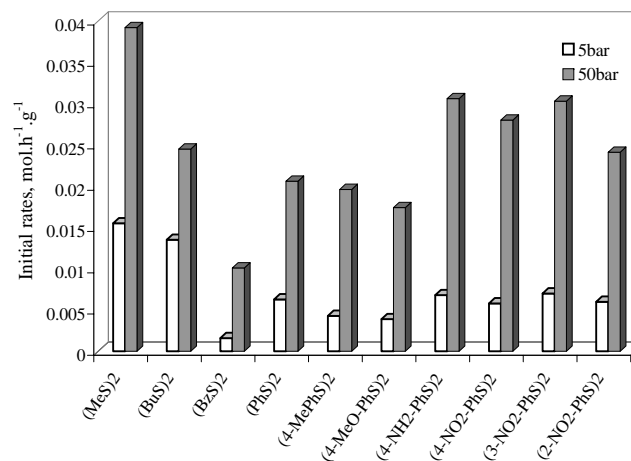


Figure 1. Initial reaction rates for the hydrogenation of disulfides at 5 and 50 bar where R = Me, Bu, Bz, Ph, 4-Me-Ph, 4-MeO-Ph, 4-NH₂-Ph, 4-NO₂-Ph, 3-NO₂-Ph, 2-NO₂-Ph. Where the aromatic substituent is -NO₂ the product is the corresponding aminothiophenol.

References

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