

## The Effect of Modifiers in Liquid Phase Hydrogenation: Use of Selective Poisons to enhance Selectivity.

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### Introduction

Selective hydrogenation of alkynes and alkadienes are important reactions that are still not fully understood. Recent studies [1] have elucidated the role of surface and sub-surface carbon and hydrogen in defining selectivity in alkyne hydrogenation. However in liquid phase systems it is often possible for there to be other molecules present or indeed the reactant molecule may have more than one functional group that can interact with the surface. In this study we have examined the effect of nitriles and amines on activity and selectivity.

### Materials and Methods

The catalyst used throughout this study was a 1 % w/w palladium on alumina supplied by Johnson Matthey. The support consisted of  $\theta$ -alumina trilobes (S.A.  $\sim 100 \text{ m}^2 \text{g}^{-1}$ ). All reactants were used without further purification. The reaction was carried out in a 0.5l Buchi stirred autoclave. 0.05 g of catalyst was added to 330 ml of degassed solvent, hexane. Reduction of the catalyst was performed *in situ* by sparging the system with  $\text{H}_2$  ( $300 \text{ cm}^3 \text{min}^{-1}$ ) for 30 minutes at 313 K while stirring the contents of the autoclave at 800 rpm. After reduction, the autoclave was adjusted to the appropriate reaction temperature of between 298 and 333 K under a nitrogen atmosphere. For 1-pentyne/pentadiene studies, 1 ml was injected into an unstirred solution, followed by 20ml of degassed hexane to ensure that all the reactant was washed into the reactor. For the competitive reactions, 1 ml of modifier was added either prior to or with the reactant. The autoclave was then mixed briefly at a stirrer speed of 800 rpm and pressurised to 1 barg with  $\text{N}_2$  and a sample was taken. The vessel was then depressurised and then pressurised with  $\text{H}_2$  to 2 barg. Following this the stirrer was set to a speed of 1000 rpm and samples taken. The liquid samples were analysed by GC. Standard checks were undertaken to confirm that the system was not under mass transport control.

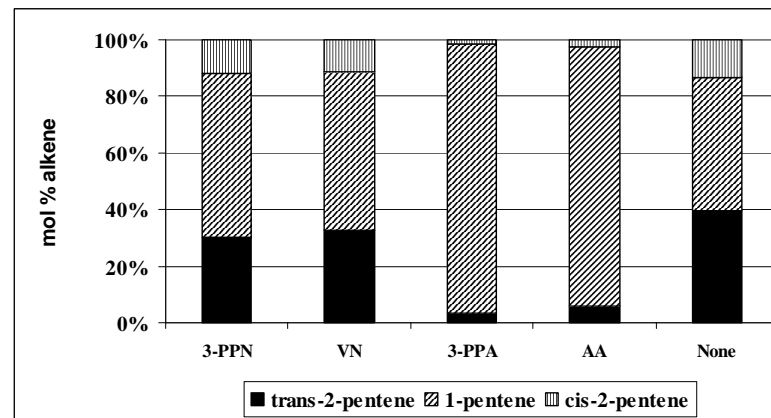
### Results and Discussion

The reactions studied were the hydrogenation of 1-pentyne and 1,3-pentadiene. Four modifiers were used, valeronitrile and its respective amine, amyl amine, and 3-phenyl propionitrile and its respective amine, 3-phenyl propylamine. These modifiers were not hydrogenated under reaction conditions. A comparison of the alkene selectivity at 50% conversion is shown in Table 1.

**Table 1. Selectivity to alkene at 50% alkyne conversion.**

Modifier	3-PPN	VN	3-PPA	AA	None
Selectivity %	68	61	87	80	57

The modifiers clearly affected the selectivity with the amines having the most significant impact, typically increasing the selectivity by 20% over that achieved by the respective nitrile. The increased selectivity to the alkenes was obtained by reducing the conversion of the alkenes to the alkane. The aromatic nitrile and amine show an enhanced effect over the aliphatic species. Identical effects are observed with the hydrogenation of 1,3-pentadiene. The effect of the modifiers on the alkene reactions is shown in Figure 1.



**Figure 1.** Alkene distribution at 50% alkyne conversion.

The addition of the modifiers significantly affects the rate of isomerisation with the amines once again having the largest impact. For the hydrogenation of 1-pentyne this allows high selectivity (>90%) to be obtained to the least thermodynamically stable alkene isomer (1-pentene).

### Significance

Classically it would be expected that the nitrile functionality would inhibit alkene reaction due to stronger adsorption, however it is the amine functionality that acts as a more effective poison due to the interaction of the lone pair with the metal.

### References

1. Teschner, D., Borsodi, J., Woosch, A., Révay, Z., Hävecker, M., Knop-Gericke, A., Jackson, S.D., and Schlögl R. *Science*, 320, no. 5872, 86 – 89, (2008).