

Friedel-Crafts Benzoylation of Anisole in Ionic Liquids

Paul Nancarrow^{1,2}, Jillian Thompson¹, David W. Rooney^{1,2}, Christopher Hardacre^{1,3}.

¹The QUILL Centre, Queen's University, Belfast BT9 5AG, Northern Ireland.

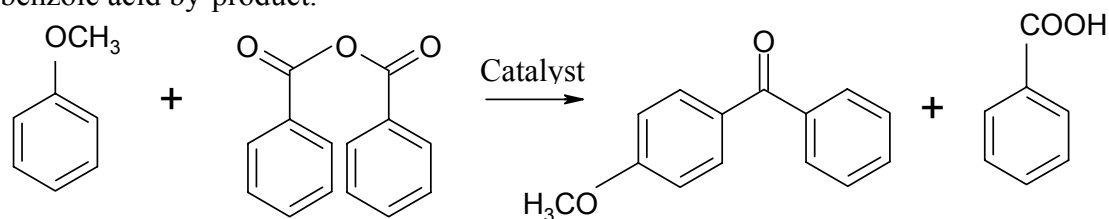
²School of Chemical Engineering, Queen's University, Belfast BT9 5AG, Northern Ireland. ³School of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland.

Introduction

The Friedel-Crafts reaction is of great importance in the specialized organic chemical industry. The products, such as aromatic ketones, are used as valuable intermediates and end products such as pharmaceuticals, agrochemicals, flavors, fragrances and fine chemicals. Agents used for Friedel-Crafts reactions are generally cheap, however overall processing costs are high due to the problems of handling of raw materials, halogenated solvents and Lewis acid activating agents (typically AlCl₃, TiCl₄, BF₃). Other catalysts used have included hydrogen fluoride [1], various metal salts supported on zeolites and clays [2], however these technologies have not solved the problems outlined.

By using ionic liquid technology coupled with a recyclable catalyst it is possible to minimize the use of volatile organic compounds and metal salt waste generation. Ionic liquids have an immeasurably low vapor pressure making them a safer alternative to organic solvents and allowing ease of separation and recycling by distillation.

The reaction (Scheme 1) chosen for investigation is the benzoylation of anisole using benzoic anhydride to produce 4-methoxybenzophenone, a UVB absorber, and benzoic acid by-product.



Scheme 1: Benzoylation of anisole using benzoic anhydride

Results and Discussion

Catalyst Screening

A number of metal triflates (In(OTf)₃, Sc, Sm, Ce, La, Y, Yb, Al, Zn, Bi, Hf) and metal triflamides (Y, Yb, Al, Zn, Ce) were screened. Hf(OTf)₄ and all the triflamide salts, were produced in house by treatment of the metal salts with the appropriate acid, HOTf or HNTf₂. The acids themselves were also screened as catalysts. All showed a very fast initial rate followed by a leveling off, similar to the profiles shown in Figure 1.

Ionic Liquid Screening

The reaction was carried out in various ionic liquids. It was found that the reaction was facilitated by $[C_n\text{mim}]PF_6$ and $[C_n\text{mim}]NTf_2$ ionic liquids whereas $[C_n\text{mim}]OTf$ and $[C_n\text{mim}]BF_4$ did not allow reaction.

Product Isolation

A number of methods of product isolation were investigated, including solvent extraction, vacuum distillation and steam stripping. It was found that solvent extraction with non-polar aliphatic compounds such as hexane was ineffective at product removal. Alkyl aromatics were able to extract the product, however, some ionic liquid was also dissolved, with an associated loss of catalyst.

Vacuum distillation required higher temperatures than expected, suggesting some interaction between the product and ionic liquid. Steam stripping caused the decomposition of the metal salts.

Deactivation of bistrifluoromethanesulfonamide catalyst

All kinetic profiles showed a very fast initial reaction leveling off to a final conversion value (Figure 1). The reaction was carried out with different catalyst loadings and it was found that the overall conversion to 4-methoxybenzophenone is directly dependent upon the catalyst loading. This pseudo-equilibrium effect occurs at low catalyst concentrations (up to ~0.5 mol%) and may be due to catalyst poisoning by trace impurities. Further research is currently under way to investigate this phenomenon.

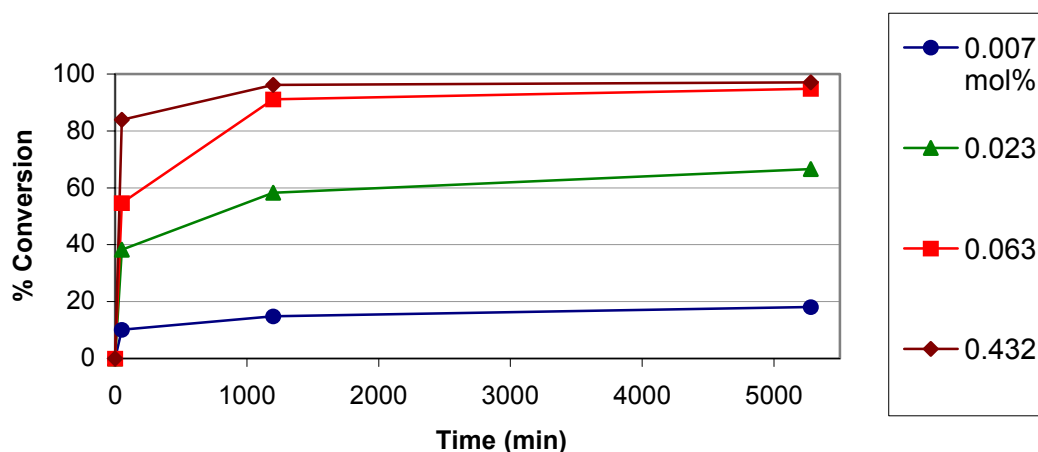


Figure 1: Some examples showing the kinetics profiles and pseudo equilibrium conversions for different HNTf₂ catalyst loadings

References

1. M. Aslam, K.G. Davenport, W.F. Stansbury, *J. Org. Chem.*, 56 (20) (1991) 5955-5958.
2. D. Barbier-Baudry, A. Dormond and F. Duriau-Montagne, *J. Mol. Catal. A-Chem.*, 149 (1-2) (1999) 215-224.