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Proposed DFT study for the N-alkylation of amines via the 'borrowing hydrogen' mechanism

Proposed DFT study for the N-alkylation of amines via the 'borrowing hydrogen' mechanism
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Amines are an important class of compounds used in the agrochemical, additives and dye industry as well as in the fine chemical industries (in the production of chemicals) and the pharmaceutical industry (many drugs contain alkylamino functions). The development of efficient and environmentally friendly methods to prepare amines has long been an important goal in organic synthesis. For various reasons, (mainly over alkylation) the synthesis of amines requires a catalyst. Traditional metal catalytic systems use precious metals such as Ir, Rh and Ru [1]. However, the major drawback of precious metal catalysts is their high cost and limited availability [1]. Recently, the focus in homogeneous catalysis is the implementation of earth-abundant metals [1]. One method of utilising earth-abundant metals for the alkylation of amines is via the borrowing hydrogen or the hydrogen auto-transfer (BH/HA) reaction (Figure 1) [2][3].

Figure 1: 'Borrowing hydrogen' or 'hydrogen auto-transfer' in the alkylation of an amine with an alcohol
This is an environmentally friendly mechanism with alcohols as alkylating agents. It has high atom efficiency, with water as the only by-product in the reaction [3]. In this DFT study, non-noble catalysts such as Cu, Co, Ni, Fe, Cr, Mn and W will be explored as earth-abundant metal catalysts in the borrowing hydrogen reaction. The aim is to predict the pathways for the hydrogen auto-transfer mechanism using these various earth-abundant metal catalysts. Preliminary calculations will identify an optimal basis set and functional that will be used in the study. All transition states will be verified by frequency and intrinsic reaction coordinate calculations. Solvation studies will be based on solvents reported in literature. From this investigation, a model will be developed to predict the reaction as well as to show the possible products from the borrowing hydrogen reaction when using a particular earth-abundant metal catalyst.

References

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