Theoretical Studies on the Hydroaminoalkylation of Alkenes with Primary and Secondary Amines

Luisa Stelter[a], Thomas Teusch[a], Jens Bielefeld[a], Sven Doye[a] and Thorsten Klüner[a]

[a] *Department of Chemistry, Carl von Ossietzky University Oldenburg, Carl-von-Ossietzky Str. 9-11, 26129, Oldenburg, Germany*
luisa.stelter@uni-oldenburg.de

Nowadays the industrial production of primary amines from alkenes requires two chemical transformations with an aldehyde as an intermediate. A waste-free alternative to this two-step process would be a hydroaminoalkylation of alkenes with methylamine. Current research results indicate that the α-alkylation of amines with alkenes catalyzed by early transition-metal complexes represents an efficient and atom economic method for the synthesis of functionalized amines from simple and easily available starting materials.[1] While the successful use of secondary amines, such as dimethylamine,[2] strongly underlines the enormous industrial potential of this reaction, the analogous intermolecular α-alkylation of primary amines, especially methylamine, remains an unsolved synthetic task to this day. Particularly worth mentioning is the fact that intramolecular α-alkylation, however, can be carried out with secondary and primary aminoalkenes.[3]
In this work, we present calculated thermodynamic data which explain these experimental findings for the first time. Based on the computed catalytic cycle several competing reactions are examined in more detail. It turns out that these are of crucial importance for the different behavior of primary and secondary amines. For these studies DFT-functionals in the program package Gaussian09.b01[4] were used.

References

1. Z. Dong, Z. Ren, S. J. Thompson, Y. Xu and G. Dong, *Chem. Rev*. **117** (2017), 9333.
2. J. Bielefeld and S. Doye, *Angew. Chem. Int. Ed.* **56** (2017), 15155; *Angew. Chem.* **129** (2017), 15352.
3. I. Prochnow, P. Zark, T. Müller and S. Doye, *Angew. Chem. Int. Ed.* **123** (2011) 6401; *Angew. Chem.* **123** (2011) 6525.
4. Gaussian 09, Revision B.01, M. J. Frisch et al., Gaussian, Inc., Wallingford CT (2010).