

# The hydrolysis of $\alpha$ -iminocarbonyls – a quantum chemical mechanistic study

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We present our DFT investigations of the hydrolysis mechanism of  $\alpha$ -iminocarbonyl compounds. The aim of the present study is to explain the experimental observations by providing a deeper understanding of the complex processes taking place in the reaction mixture.

The  $\alpha$ -arylation of  $\alpha$ -aminocarbonyl compounds can be achieved through oxidative deprotonation with transition-metal catalysts. In a one-pot reaction a 1,2-dioxo compound can be obtained in the presence of copper(II) chloride catalyst, atmospheric oxygen and an excess amount of TBHP through an imine intermediate. [1] Remarkably, modification of the reaction conditions leads to the formation of the  $\alpha$ -iminocarbonyl derivate. It has been also shown that the catalyst, the oxidizing agent and the presence of air can enhance the hydrolysis in a synergistic fashion.

Our calculations have revealed two possible mechanisms for the imine hydrolysis: a catalytic route by  $\text{CuCl}_2$  and an oxidative mechanism with TBHP. Along the catalytic route  $\text{CuCl}_2$  plays a twofold role: it acts as a Lewis acid and also as a catalyst for autoprotolysis. On the oxidative path TBHP acts as an OH-radical source which induces radical pathways. Our findings also explain the observed synergistic effect: the oxidant regenerates the copper catalyst from its complexated form by oxidizing the aromatic amine derivatives whereas the copper salts catalyze the formation of the hydroxyl radicals.

[1] Wu, J.-C., Song, R.-J., Wang, Z.-Q., Huang, X.-C., Xie, Y.-X., Li, J.-H. *Angew. Chem. Int. Ed.*, 51:3453-3457, 2012.