A Combination of DFT and Spectroscopy Solves Photocatalytic Mechanisms: the Case of N–O bonds

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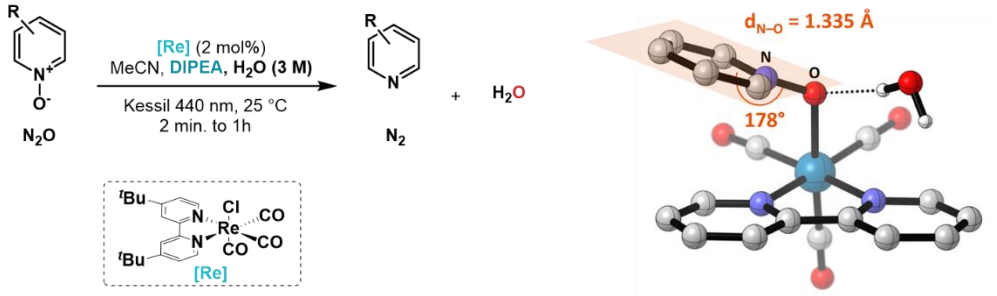
The accumulation of nitrogen oxides in the environment calls for new pathways to interconvert the various oxidation states of nitrogen, and especially their reduction. However, the large spectrum of reduction potentials covered by nitrogen oxides makes it difficult to find general systems capable of efficiently reducing various *N*-oxides. Nitrous oxide N_2O is a thermodynamic oxidant but has a very low reactivity; on the contrary, pyridine N-oxide is an organic substrate with a more challenging reduction potential. We developed in the group a new pathway that enables to reduce both N_2O back to nitrogen and pyridine N-oxide to pyridine at room temperature by means of photocatalysis using [Re(bpy)(CO)$_3$Cl], traditionally used to deoxygenate CO_2. Herein, the mechanism of the N–O bond deoxygenation will be described for both substrates. It used a combination of multiple techniques, including laser flash photolysis, spectroelectrochemistry, NMR and infrared spectroscopy, together with computational studies (DFT).



References

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