

To Bend or Not to Bend: Is CO₂ Bending Required to Promote its Reduction? [1]

Nicolas, E.; von Wolff, N.; Cantat, T.

LCMCE, NIMBE, CEA, CNRS, Université Paris-Saclay, France

CO₂ reduction is a process actively investigated in order to use CO₂ as a C₁ feedstock for the chemical industry, yet this process is thermodynamically and kinetically challenging.[2] While electrochemical studies, together with the analysis of the Walsh diagram of CO₂, proposed that bending the O–C–O angle is a requirement to promote the reduction of CO₂, this approach is only valid for single electron transfer (SETs) reactions. This paradigm does not apply to hydride-transfer-mediated reductions, for which new rules need to be devised.

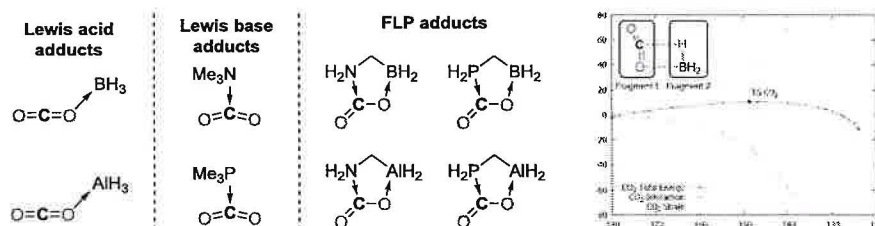


Figure 1 Adducts investigated (left); Example of ASM results (right)

We propose here the use of the Activation Strain Model (ASM) as developed by Bickelhaupt *et al.*[3] to probe the reduction of CO₂ by BH₃, with or without added organocatalysts, which leads to a decorrelation of the respective influences of electronic and steric parameters. We found that slight bending is indeed beneficial to promote CO₂ reduction, but that strong bending is detrimental to the process. Keys for the design of an optimal catalyst are provided.

[1] Nicolas, E.; von Wolff, N., Cantat, T., *Submitted*.

[2] Aresta, M. In *Carbon Dioxide and Organometallics*; Xiao-Bing, L., Ed.; Springer International Publishing, 2016

[3] Wolters, L. P., Bickelhaupt, F. M.; *WIREs Comput. Mol. Sci.* 5, 324 (2015).

E-mail: emmanuel.nicolas@cea.fr

www: <http://iramis.cea.fr/Pisp/thibault.cantat/>