# Computational study of glycerol/guanidine associative system for CO_2 capture

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The excess of atmospheric CO_2 is a problem that has been causing harsh climatic changes, needing the urgent control of its emission and capture. To that purpose, the chemical absorption with alcohols and amines has been largely in use [1]. According to experimental [1] and theoretical [2] works, guanidine, a strong base, is a promising CO_2 scavenger. Alternatively, biofuels – produced from vegetable oils - is also a way to reduce its atmospheric concentration through photosynthesis. [3] However the byproduct, glycerol (propanetriol), has low industrial application [4]. Towards this problematic and knowing that the associative use of strong bases with polyols has been studied for CO_2 capture [5], the present work aims to investigate the possible pathways and energetic profiles involved in the CO_2 scavenging. Three possible systems were identified, which are shown in **Figure 1**.
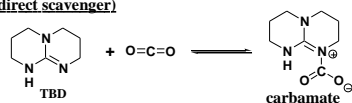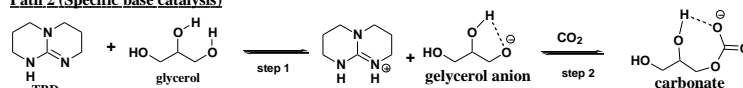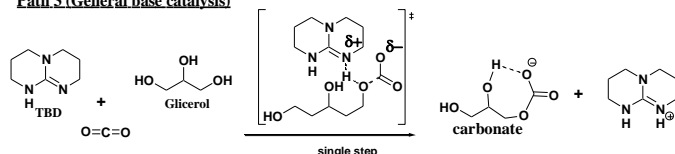

Figure 1. Possible paths to CO_2 capture with the system guanidine-glycerol.

DFT CAM-B3LYP/6-311++g(2d,2p) method was selected after trial with different functionals compared to reference methods   a similar system [2]. Polar media was

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simulated with IEFPCM, using water as solvent. In **path 1**, different guanidines were investigated to identify the molecular properties important for the capture. Among them, **TBD** showed the best energetic profile, suggesting that intramolecular hydrogen bond (IHB) is more important than possible π-electron delocalization (**Figure 2**). However, although CO_2 concentration is reduced by guanidines, the carbamate intermediate may not be isolated, probably due to decomposition *in situ*.
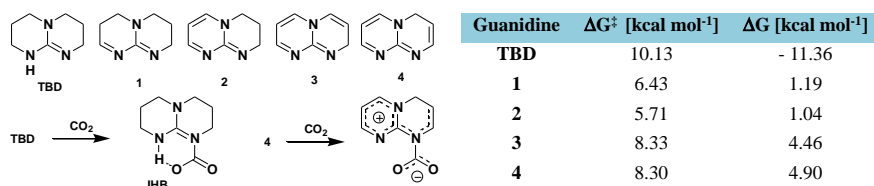
Guanidine	$\Delta G^{\ddagger}$ [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TBD	10.13	- 11.36
1	6.43	1.19
2	5.71	1.04
3	8.33	4.46
4	8.30	4.90

Figure 2. Energetic data to CO_2 capture with different guanidines at 298 K

In **path 2**, the conformational analysis of glycerol and its anions indicated that deprotonation of primary hydroxyl is energetically preferred, with the anion establishing two IHBs. In **step 1**, a positive Gibbs free energy change was observed ($\Delta G^{298} = 7,69$ kcal mol^{-1}). In **step 2**, CO_2 is spontaneously captured by glycerol anion ($\Delta G^{298} = -12,73$ kcal mol^{-1}) with no activation barrier.

Calculations are still being made to find the concerted transition state of single step (**Path 3**).

Key-words: Carbon dioxide, capture, glycerol, DFT.

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