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Modeling a Menshutkin S_N2 Chemical Reaction Inside Carbon Nanotubes

The kinetics and thermodynamics of chemical reactions can alter drastically when bulk conditions change from gas-phase into polarizable media as, for instance, single-walled carbon nanotubes (SWNTs). In fact, they have shown the ability to catalyze chemical reactions when they occur in their inner space[1,2]. To date, no systematic investigation has considered the effect of radius and chirality on the kinetics of reacting systems. The present work is a computational study that sheds some light on this issue by comparing the impact of different types of SWNTs, namely *armchair*(n,n), *zigzag*(n,0) and *chiral*(n,m), on the particular Menshutkin S_N2 reaction between ammonia and chloromethane. The calculations have been performed at the quantum mechanical Density Functional Theory (DFT) level, using the functional M06-2X and double-zeta basis sets of atomic functions.

In general, all the SWNTs are able to reduce significantly the activation energy and the endothermicity of the reaction when compared to the values in gas-phase. For large diameters, all types of SWNTs converge to the limit values of these two energetic parameters, respectively, 28 kcal.mol^{-1} and 21 kcal.mol^{-1}, which correspond to the reaction over a graphene surface. However, as the diameters decrease, each type of SWNT shows a different potential well, with chiral (6,4) SWNT (diameter 6.8 Å) exhibiting the lowest energy barrier of 17.9 kcal.mol^{-1}.
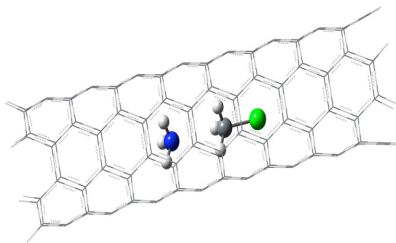
Figures

Figure 1: SWNT with S_N2 Menshutkin reactants.

References

[1]   Halls, M. D.; Schlegel, H. B., J. Phys. Chem. B, 106 (2002) 1921.

[2]   Giacinto, P.; Bottoni, A.; Calvaresi, M.; Zerbetto, F., J. Phys. Chem. C, 118 (2014) 5032