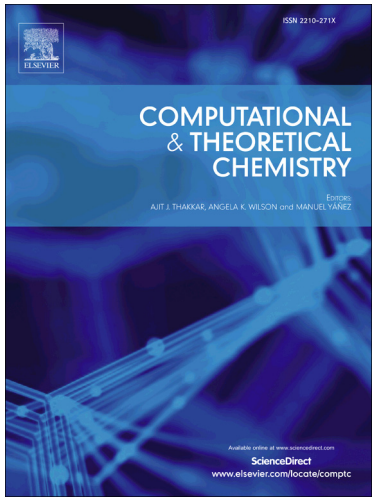

Theoretical prediction on CO insertion reactions through the anionic complex $[ClMg(\eta^2\text{-}O_2C]^-$ as a catalyst

Jin-Feng Ma, Fang Ma, Zhong-Jun Zhou, Ying-Tao Liu

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Theoretical prediction on CO insertion reactions through the anionic complex $[ClMg(\eta^2\text{-}O_2C]^-$ as a catalyst

Jin-Feng Ma [a], Fang Ma [a, *], Zhong-Jun Zhou[b], Ying-Tao Liu[c]

[a]School of Chemistry and Materials Science, Huaibei Normal University, Huaibei 235000, (P. R. China)

Corresponding author： E-mail address: mafangchem@foxmail.com (F. Ma).

[b]Institute of Theoretical Chemistry, Jilin University, Changchun,130023 (P. R. China)

[c]Department of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750012 (P. R. China)

The mechanisms of the reaction of CO inserting into the C-H bond of furane/thiofuran through the anionic magnesium–CO_2 complex $[ClMg(\eta^2\text{-}O_2C)]^-$ as a reaction catalyst are investigated using the second-order Møller-Plesset (MP2), and the polarized continuum model (PCM) is applied to simulate the solvent effects. Calculated results show that the insertion reaction route includes three steps:(i) the dehydrogenation of furane/thiofuran through the capturing of the anion complex $[ClMg(\eta^2\text{-}O_2C)]^-$ with strong carbene character, resultes in an intermediate **I**, (ii) the addition of CO via the C-C bond formation between the carbon atom of **I** and the carbon atom of CO through the partial negative charge transfer into the π^* orbital of CO, forms an anion species **III**, and (iii) H abstraction from the neutral complex $[ClMg(\eta^2\text{-}O_2CH)]^0$ produces the aldehyde product. We find that the reactions of CO inserting into the C-H bond of furane/thiofuran is an endothermic process, and the H abstraction to form aldehyde species (correponding transition states **TS3)** is the rate-determining step. Meanwhile, solvent effect is important for the CO insertion reaction, for example, the barrier of **TS3** in THF solvent is lower by 5kcal/mol than corresponding that in acetone solvent. We expected that the understanding of the insertion reaction can provide valuable insights into related reactions.

Keywords: carbene character, CO insertion reaction, C-C bond formation, reaction mechanism, solvent effect