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Theoretical prediction on CO insertion reactions through the anionic complex $[\text{ClMg}(\eta^2\text{-O}_2\text{C})^-]$ as a catalyst

Jin-Feng Ma^a, Fang Ma^{a,*}, Zhong-Jun Zhou^b, Ying-Tao Liu^c

^aSchool of Chemistry and Materials Science, Huaibei Normal University, Huaibei 235000, (P. R. China)

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

^bInstitute of Theoretical Chemistry, Jilin University, Changchun, 130023 (P. R. China)

^cDepartment 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-CO₂ complex $[\text{ClMg}(\eta^2\text{-O}_2\text{C})^-]$ 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 $[\text{ClMg}(\eta^2\text{-O}_2\text{C})^-]$ with strong carbene character, results 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 $[\text{ClMg}(\eta^2\text{-O}_2\text{CH})]^0$ 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 (corresponding 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

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