

On the Reaction Mechanism of the Complete Intermolecular O₂ Transfer between Mononuclear Nickel and Manganese Complexes with Macrocyclic Ligands

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Abstract

The recently described intermolecular O₂ transfer between the side-on Ni-O₂ complex [(12-TMC)Ni-O₂]⁺ and the manganese complex [(14-TMC)Mn]²⁺, where 12-TMC and 14-TMC are 12- and 14-membered macrocyclic ligands, 12-TMC=1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane and 14-TMC=1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, is studied by means of DFT methods. B3LYP calculations including long-range corrections and solvent effects are performed to elucidate the mechanism. The potential energy surfaces (PESs) compatible with different electronic states of the reactants have been analyzed. The calculations confirm a two-step reaction, with a first rate-determining bimolecular step and predict the exothermic character of the global process. The relative stability of the products and the reverse barrier are in line with the fact that no reverse reaction is experimentally observed. An intermediate with a $\mu\text{-}\eta^1\text{:}\eta^1\text{-O}_2$ coordination and two transition states are identified on the triplet PES, slightly below the corresponding stationary points of the quintet PES, suggesting an intersystem crossing before the first transition state. The calculated activation parameters and the relative energies of the two transition states and the products are in very good agreement with the experimental data. The calculations suggest that a superoxide anion is transferred during the reaction.

keywords

Activation Parameters; Biomimetic Complexes ; Density Functional Calculations; O₂ Transfer Reaction; Pes Analysis