

Theoretical Investigation of Catalytic Hydrocarboxylation of Olefins with CO₂

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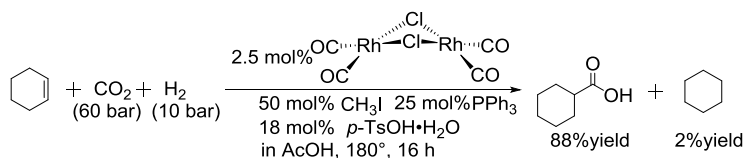
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[Abstract] Carboxylic acids can be directly formed from CO₂, H₂, and simple olefins by using rhodium(I) catalyst. In this reaction, the addition of iodide compounds, such as CH₃I, is indispensable to increase the yield of the product. To understand the role of the iodide additives, we studied the mechanism of the catalytic hydrocarboxylation of cyclohexene with CO₂ and H₂ by using an automated reaction search method, called multi-component artificial force induced reaction (MC-AFIR) method. The reaction can be divided into two parts. First, CO and H₂O is obtained from CO₂ and H₂ through the formation of formic acid. Then, the CO and olefin convert to the carboxylic acid. The iodide additive plays two important roles. One is the formation of cyclohexyl iodide to promote the oxidative addition to the rhodium(I) catalyst. Another is the stabilization of intermediates and transition states through the interaction with phosphine ligands.

[Introduction] The CO₂ is an attractive C1 building block which leads carboxylic acids and their derivatives. To establish the catalytic systems to form the carboxylic acids from



Scheme 1. Catalytic hydroxycarbonylation of olefins with CO₂ and H₂ catalyzed by the rhodium complex.[1]

CO₂, the mechanical understanding is indispensable. Leitner *et al.* reported an effective catalytic system for the hydroxycarbonylation of simple olefin with CO₂ and H₂ leading the carboxylic acid as shown in Scheme 1.^[1] Several experimental measurements were performed to discuss the mechanism of this catalytic system. First, it was found that the carboxylic group was constructed not by CO₂ but by CO and H₂O according to the nuclear magnetic resonance spectroscopy. Second, the yield of the carboxylic acid increased dramatically by the addition of iodide compounds, such as CH₃I. Third, the formation and consumption of cyclohexyl iodide was observed by the mass spectrometry, which implied that the role of the CH₃I additive was the conversion of cyclohexene to cyclohexyl iodide and cyclohexyl iodide could be a reactant instead of cyclohexene. Forth, to discuss the effect of the intermediates, the same reaction starting from other reactants, such as cyclohexyl iodide, cyclohexanol, and cyclohexyl acetate, were performed. Contrary to the expectation, the product yield depended on the reactant. Cyclohexanol and cyclohexyl acetate provided high product yield as cyclohexene. Whereas, the product yield starting from cyclohexyl iodide was only 21 %, even though cyclohexyl iodide was assumed to be formed and consumed during the catalytic

reaction. To get the more detailed insights of this catalytic system, we performed one of the methods in the Global Reaction Route Mapping (GRRM) strategy, called the artificial force induced reaction (AFIR) method,^[2] to search systematically all possible reaction pathways. In this study, we also discuss about the role of iodide additives and the reason of the product yield dependency on the reactants based on the calculated Gibbs free energy profile.

[Methods] First, approximate reaction pathways were explored by the MC-AFIR method, in which the AFIR functions were minimized with $\gamma = 300\text{-}400 \text{ kJ mol}^{-1}$. The initial AFIR search was carried out at M06-L/Def2SV level of theory. Then, all the obtained approximate local minima and transition states (TSSs) were re-optimized without artificial force at the B3LYP-D3/SDD (for Rh and I) and 6-31g(d) (for other atoms) levels. Single point energies were calculated at B3LYP-D3/SDD (for Rh and I); 6-31+g(d,p) (for other atoms) levels of theory. The solvation free energy was included by the PCM model with a dielectric constant of 6.3 (acetic acid) for all the calculations. The intrinsic reaction coordinate (IRC) was calculated to confirm the reaction pathway. All these AFIR search, optimizations and IRC calculations were performed with the GRRM program^[3] using energies, first, and second energy derivatives computed with the Gaussian09 program.

[Results and Discussion] The reaction system can be divided into two catalytic cycles. One is for the formation of CO and H₂O from CO₂ and H₂ (Cycle I) and the other cycle is for the producing the carboxylic acid from CO and olefin (Cycle II). The Cycle I starts from the oxidative addition of H₂ to the Rh(I) complex, followed by the CO₂ insertion. Thus, we firstly investigated about the stability and the catalytic ability of the mononuclear Rh(I) complexes with different number of PPh₃ ligands (RhCl(CO)_n(PPh₃)_m; $n, m = 0, 1, 2$). The reaction barrier of the oxidative addition of H₂ depended on the coordination number of phosphine ligands. The most favorable pathway started from the dissociation of the phosphine ligand from the Vaska-type Rh(I) complex RhCl(CO)(PPh₃)₂, followed by the oxidative addition of H₂. The intermediate after the dissociation of the phosphine ligand RhCl(CO)(PPh₃) was stabilized by the interaction energy between CH₃I and the phosphine. Next, the insertion of CO₂ to the Rh(I) complex and the carbonylation took place. Then, the CO₂ and H₂ in the Rh(I) complex converted to formic acid, which can be decomposed into CO and H₂O. Although, the formation of CO and H₂O from CO₂ and H₂ (Cycle I) was the endothermic reaction, this catalytic reaction could take place because of the exothermicity of the following Cycle II.

The Cycle II started from the formation of the cyclohexyl iodide from cyclohexene and CH₃I to promote the following oxidative addition to the Rh(I) catalyst. Then, the insertion of the CO, which was obtained from the Cycle I, took place, followed by the transformation leading to the desired carboxylic acid. The rate-determining step (RDS) of the overall catalytic process was the carbonylation step in Cycle I, with an activation barrier of 33.7 kcal mol⁻¹.

In this presentation, we will show the reaction pathways starting from other substrates, such as cyclohexanol, cyclohexyl acetate, and cyclohexyl iodide and discuss about the reason of the dependence of the product yield.

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[References]

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