Mechanistic study on hydroxycarbonylation of cycloalkene using homogeneous rhodium catalysts with PPh_3 ligand

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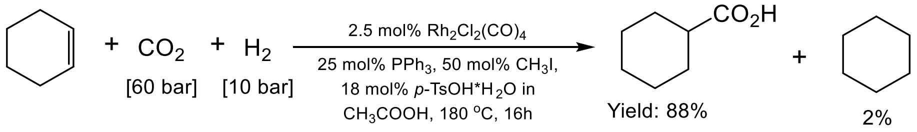
Abstract: The reaction mechanism of the hydroxycarbonylation of cyclohexene with formic acid to form cyclohexanecarboxylic acid using organorhodium complexes was investigated both experimentally and computationally. It was found that excess CH_3I and PPh_3 promote this reaction. The active catalyst species was determined to be a five-coordinated rhodium hydride 16-electron complex derived from a mononuclear rhodium 16-electron complex (Vaska-type complex). The addition of PPh_3 contributed to the formation and stabilization of active rhodium complexes and CH_3I promoted elimination of the PPh_3 ligand from the Vaska-type complex and simultaneously induced the catalytic active species.

Keywords: CO_2, formic acid, hydroxycarbonylation, organorhodium complex, reaction mechanism

1. Introduction

The CO_2 is an attractive C1 building block which leads carboxylic acids and their derivatives. Recently, Leitner et al. reported that saturated carboxylic acids can be obtained in high yield from various alkenes and CO_2/H_2 in the presence of organorhodium complex as shown in Scheme 1.[1]



Scheme 1. Hydroxycarbonylation of alkenes with CO_2/H_2 using organorhodium complex.[1]

Leitner et al. proposed that the reaction system of the hydroxycarbonylation comprised with two catalytic cycles; i.e., cycle **I**) the reverse water gas shift reaction (rWGS) to form CO/H_2O from CO_2/H_2, cycle **II**) the carbonylation of Rh-alkyl complex species by CO (rWGS) to produce the carboxylic acid. However, the details of the two catalytic cycles remain unknown as no direct information related to the Rh complex as the active species was obtained during this reaction. Here, we report the details of the reaction mechanism and identify the active species of the catalyst by combining experimental and computational methods and clarify the role of each promoter.[2]

2. Experimental

2.1. Typical reaction procedure

Under N_2 atmosphere, 0.14 mmol of $[\{RhCl(CO)_2\}_2]$, 2.77 mmol of CH_3I, 100 mmol of CH_3COOH, 21 mmol of HCOOH, 1 mmol of *p*-$TsOH{\cdot}H_2O$, 5.70 mmol of cyclohexene and 1.37 mmol of PPh_3 were charged into the 30 ml pressure vessel. The hydroxycarbonylation reaction was carried out at 180 °C for 2.5 or 5 hours in a batch manner. After being cooled to room temperature, the reaction mixture was analyzed by GC and GC-MS.

2.2. 31P NMR measurements

A Bruker AVANCE-III high-resolution spectrometer (400MHz for ^{1}H) was used for all the NMR experiments.

2.3. Computational analysis

All the computations employed in this study performed using the density functional theory (DFT) combined with the Global Reaction Route Mapping (GRRM) strategy,[3] called the artificial force induced reaction (AFIR) method,[4] to search systematically all the possible reaction pathways systematically.

3. Results and discussion

The hydroxycarbonylation of cyclohexene with HCOOH afforded cyclohexanecarboxylic acid in good yield (83%) with small amount of iodocyclohexane, acetoxycyclohexane, and cyclohexane. This result was almost same as original reaction results using CO_2/H_2 instead of HCOOH as expected. It seems that iodocyclohexane and acetoxycyclohexane would be intermediates of cyclohexanecarboxylic acid. When phosphonium iodide $[Ph_3P(CH_3)]I$ was used instead of PPh_3 and CH_3I, the yield of cyclohexanecarboxylic acid improved as the ratio of $[Ph_3P(CH_3)]I$ to $[\{RhCl(CO)_2\}_2]$ increased. Moreover, $RhCl(CO)(PPh_3)_2$ was also usable as a catalyst for this reaction. Surprisingly, cyclohexanecarboxylic acid was also observed in lower yield (9%) under the same conditions except for non-use of any Rh species. It should be noted that significant amounts of iodocyclohexane (9%) and acetoxycyclohexane (22%) were detected in this control experiment. As the results of the NMR experiments, it was confirmed that $[Ph_3P(CH_3)]I$ was generated from PPh_3 and CH_3I, and $RhCl(CO)(PPh_3)_2$ was detected in the model reaction of $[\{RhCl(CO)_2\}_2]$ with PPh_3. Furthermore, the addition of CH_3I promoted the elimination of the PPh_3 ligand from $RhCl(CO)(PPh_3)_2$. Based on these results, the catalytic reaction mechanism for the hydroxycarbonylation of cyclohexene can be proposed (Figure 1).

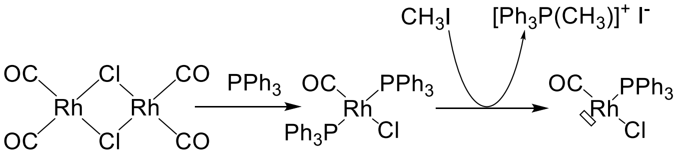


Figure 1. The role of PPh_3 and CH_3I

4. Conclusions

The overview of the reaction mechanism and the role of each component were clarified now. The active catalyst species was determined to be a five-coordinated rhodium hydride 16-electron complex $[Rh(H)(X)(CO)(PPh_3)_2$, (X=Cl or I)] derived from the Vaska-type intermediate. PPh_3 and CH_3I played the following roles: i) to promote the formation of the Vaska-type complex from $[\{RhCl(CO)_2\}_2]$, ii) to aid the elimination of the PPh_3 ligand from the Vaska-type complex by stabilizing the free energy of formation of a mononuclear three-coordinated rhodium 14-electron complex through the formation of $[Ph_3P(CH_3)]I$, and iii) to generate the active rhodium hydride species.

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References

1. T.G. Ostapowicz, M. Schmitz, M. Krystof, J. Klankermayer, W. Leitner, Angew. Chem. Int. Ed. 52 (2013) 12119–12123.
2. T. Oku, M. Okada, M. Puripat, M. Hatanaka, K. Morokuma, J.-C. Choi, J. CO_2 Util. 25 (2018) 1–5
3. GRRM14: S. Maeda, Y. Harabuchi, Y. Osada, T. Taketsugu, K. Morokuma, and K. Ohno, http://iqce.jp/GRRM/index_e.shtml.
4. S. Maeda, K. Ohno, K. Morokuma, Phys. Chem. Chem. Phys. 15 (2013) 3683–3701.