Journal of CO_2 Utilization 25 (2018) 1–5

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

journal homepage: www.elsevier.com/locate/jcou

Promotional effect of CH_3I on hydroxycarbonylation of cycloalkene using homogeneous rhodium catalysts with PPh_3 ligand

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ARTICLE INFO

Keywords:
CO_2
Formic acid
Hydroxycarbonylation
Organorhodium complex
Reaction mechanism

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). PPh_3 and CH_3I played the following roles: i) to promote the formation of the Vaska-type Rh complex from $Rh_2Cl_2(CO)_4$ (**1**), 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 phosphonium iodide ($[Ph_3P(CH_3)]I$), and iii) to generate the active rhodium hydride species.

1. Introduction

Reactions that use CO_2 as a C1-building block to convert it into useful chemicals have attracted significant attention from the viewpoint of the utilization of unused resources as well as environmental problems [1–6]. Traditionally, such reactions have used been in industrial methods, such as those for the synthesis of urea from CO_2 and NH_3 and the synthesis of salicylic acid or *p*-hydroxybenzoic acid by the "Kolbe-Schmitt reaction" [7,8]. However, the use of CO_2 is limited because of its stability and relatively poor reactivity. Since Noyori, Ikariya, and Jessop et al. reported in 1994 that formic acid (HCOOH) or *N*,*N*-dimethylformamide (DMF) and methyl formate can be synthesized by the hydrogenation of supercritical CO_2 using an organoruthenium catalyst [9–15], CO_2 reduction reactions have been studied actively. 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 an organorhodium complex (Scheme 1) [16].

Leitner et al. have successfully developed a system for the hydroxycarbonylation of alkenes with very high efficiency by using the appropriate catalyst precursor and ligand, through the optimization of the promoter, CH_3I, as well as the reaction conditions [16]. However, the hydrogenation of cyclohexene to cyclohexane was a serious side reaction of this system. Based on the results of both labeling experiments performed using $CO_2 + D_2$, $^{13}CO_2 + H_2$, $CO_2 + H_2 + H_2{}^{18}O$ isotopes and the control experiment using CO instead of CO_2, it was determined that the formation of Rh-alkyl species was a key factor and that both a catalytic cycle of the reverse water gas shift reaction (rWGS) and a parallel carbonylation cycle of Rh-alkyl by CO (from rWGS) to generate a Rh-acyl species were associated with each other [16]. The desired saturated carboxylic acid was produced by the hydrolysis of the acyl intermediate. However, the details of the two proposed cycles remain unknown as no direct information related to the Rh complex as the active species was obtained during this reaction, and only a rhodium iodide cluster was produced after the treatment of the reaction solution in air. 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. In this study, cyclohexene was used as the reaction substrate

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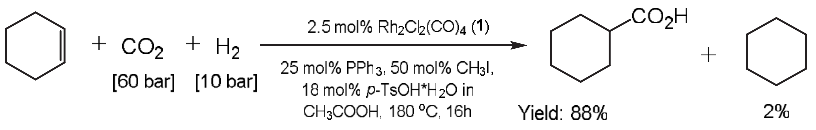
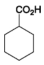
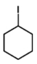
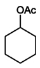
https://doi.org/10.1016/j.jcou.2018.02.015
Received 13 November 2017; Received in revised form 16 February 2018; Accepted 24 February 2018



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

Table 1
Hydroxycarbonylation of cyclohexene with HCOOH and CO_2/H_2.

Entry	Cat.	C1 source	t (h)	Additive	mol ratio[a]		Conv.[b]	Yield (%)[c]			
					P/Rh	CH_3I/Rh	(%)				
1	**2**	HCOOH[d]	2.5	CH_3I and PPh_3	5	10	94	79	4	1	1
2	**2**	HCOOH[d]	2.5	$[Ph_3P(CH_3)]I$	3	1	67	9	0	25	1
3	**2**	HCOOH[d]	2.5	$[Ph_3P(CH_3)]I$	4.5	2.5	89	77	1	3	1
4	**2**	HCOOH[d]	2.5	$[Ph_3P(CH_3)]I$[e]	7	5	84	76	1	2	1
5	**2**	HCOOH[d]	2.5	$[Ph_3P(CH_3)]I$[e] and CH_3I	7	10	94	82	2	1	1
6	**1**	HCOOH[d]	5.0	CH_3I and PPh_3	5	10	97	84	2	0	1
7	**1**	HCOOH[d]	2.5	$[Ph_3P(CH_3)]I$	0.5	0.5	62	10	1	17	0
8	**1**	HCOOH[d]	2.5	$[Ph_3P(CH_3)]I$	2.5	2.5	64	27	2	19	2
9	**1**	HCOOH[d]	2.5	$[Ph_3P(CH_3)]I$[e]	5	5	85	61	2	5	1
10	**1**	HCOOH[d]	2.5	$[Ph_3P(CH_3)]I$[e] and CH_3I	5	10	88	74	2	1	2
11	**2**	CO_2/H_2[f]	2.5	CH_3I and PPh_3	5	10	91	48	10	4	7
12	**2**	CO_2/H_2[f]	2.5	$[Ph_3P(CH_3)]I$	3	1	61	6	2	16	16
13	**2**	CO_2/H_2[f]	2.5	$[Ph_3P(CH_3)]I$	4.5	2.5	75	32	4	11	12
14	**2**	CO_2/H_2[f]	2.5	$[Ph_3P(CH_3)]I$	7	5	80	41	4	8	7
15	**2**	CO_2/H_2[f]	2.5	$[Ph_3P(CH_3)]I$ and CH_3I	7	10	88	51	10	7	5
16	**1**	CO_2/H_2[f]	2.5	CH_3I and PPh_3	5	10	90	52	11	4	6
17	**1**	CO_2/H_2[f]	2.5	$[Ph_3P(CH_3)]I$	0.5	0.5	48	3	2	21	1
18	**1**	CO_2/H_2[f]	2.5	$[Ph_3P(CH_3)]I$	2.5	2.5	48	4	5	20	2
19	**1**	CO_2/H_2[f]	2.5	$[Ph_3P(CH_3)]I$	5	5	58	20	6	16	3
20	**1**	CO_2/H_2[f]	2.5	$[Ph_3P(CH_3)]I$ and CH_3I	5	10	76	30	11	8	5

Reaction conditions: $T = 453$ K, 5.7 mmol of cyclohexene, 100 mmol of CH_3COOH, 1.0 mmol of p-TsOH·H_2O, and 0.28 mmol of Rh as mononuclear complex in 30-ml pressure vessel; [a]Total mol number of free PPh_3 and coordinated PPh_3 ligand in Rh source complex *vs.* that of Rh as mononuclear complex; [b]Conversion rate of cyclohexene; [c]GC yield using internal standard; [d]21 mmol of HCOOH; [e]1.36 mmol of $[Ph_3(CH_3)P]I$ (*i.e.*, same amount of $[Ph_3P(CH_3)]I$) was used in entries 4, 5, 9, and 10; [f]290 mmol of CO_2 and 12 mmol of H_2 (*i.e.* initial pressure is approximately 13 MPa at 453 K).

while formic acid was used as an equivalent of the CO_2/H_2 mixed gas, in order to simplify both the reaction and its analysis. It was determined that formic acid has the following effects: i) it allows for the highly selective synthesis of the desired compound by suppressing the hydrogenation of the alkenes and ii) it results in a safe and efficient reaction system that does not require the use of high-pressure or explosive gases. Moreover, it is expected that the reaction system will be more efficient because it will not compete with the active rhodium species during the two catalyst cycles.

2. Materials and methods

2.1. General procedures

All the manipulations were performed in an atmosphere of purified nitrogen. Iodomethane (CH_3I), acetic acid (CH_3COOH), formic acid (HCOOH), and p-toluenesulfonic acid monohydrate (p-TsOH·H_2O) were purchased from Wako Pure Chemical Industries Co. Cyclohexene was purchased from Tokyo Chemical Industry Co. Triphenylphosphine (PPh_3) was purchased from Sigma-Aldrich Co. Hydrogen (99.99999%) and carbon dioxide (99.999%) were used without further purification. The reaction products were identified by GC–MS analysis (GCMS-QP2010SE, Shimadzu Co.; TC-FFAP, GL Sciences). The selectivity and chemical yield of the products were determined by GC analysis (GC-2025, Shimadzu Co.; FID detector and TC-FFAP capillary column, GC Sciences). The conversion of HCOOH was evaluated by GC-TCD analysis (GC-2014, Shimadzu Co.; TCD detector and TSG–1 packed column, SHINCARBON A 60–80).

2.2. Typical reaction procedure

$Rh_2Cl_2(CO)_4$ (**1**) (54 mg, 0.14 mmol), CH_3I (393 mg, 2.77 mmol), CH_3COOH (6.0 g, 100 mmol), HCOOH (0.97 g, 21 mmol), p-TsOH·H_2O (190 mg, 1 mmol), cyclohexene (468 mg, 5.70 mmol), and PPh_3 (359 mg, 1.37 mmol) were introduced into a 30-ml pressure vessel (Tvs-N2, Taiatsu Techno). The hydroxycarbonylation reaction was carried out at 180 °C for 2.5 or 5 h in a batch manner. After being cooled to room temperature, the product solution was analyzed by GC and GC–MS.

2.3. ^{31}P NMR measurements

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

2.4. Computational analysis

All the computations employed in this study performed using the density functional theory (DFT) with the B3LYP-D3 functional [17–19]. The solvation effect was accounted for by using the polarized continuum model (PCM) [20] with a dielectric constant of 6.2528 (acetic acid). Geometry optimizations were performed by using the Stuttgart-Dresden (SDD) basis set with the associated effective core potential [21] for rhodium and the 6-31G(d) basis sets [22] for the other materials (BS1). The Gibbs free energy corrections at 180 °C and 69.085 atm were obtained at the same level of theory. Single-point calculations were performed after the geometry optimizations using larger basis sets, namely, SDD and 6-31 + g(d,p) for rhodium and the other materials, respectively (BS2). All the calculations were carried out *via* the global