Ruthenium complex-catalyzed hydroformylation of alkenes with carbon dioxide

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Abstract
Carbon dioxide can be used as a reactant for the hydroformylation of alkenes. The ruthenium complexes derived from H₄Ru₄(CO)₁₂ and LiCl effectively catalyze the hydroformylation of cyclohexene with CO₂ to give hydroxymethylcyclohexane with a yield of 88%. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydroformylation of alkenes (oxo-reaction) is one of the most important commercial examples of homogeneous catalysis with transition metal complexes. More than six million tons of aldehydes and alcohols are produced annually in this manner [1]. As a C₁ molecule, CO₂ has the advantages of nontoxicity and abundancy, which CO does not have. However, little is known about its utilization in the syntheses of aldehydes and alcohols because of its low reactivity towards alkenes. Now, our idea is the transformation of CO₂ to CO and the subsequent hydroformylation of alkenes using the CO formed. As for the first step, we previously reported that ruthenium cluster complexes effectively catalyze the hydrogenation of CO₂ to CO in the presence of halide salts [2–4]. To our surprise, some alkenes are found to be excellent substrate for the hydroformylation with CO₂ catalyzed by Ru carbonyl clusters and alkaline metal halides, not being simply hydrogenated to alkanes. This means that CO₂ hydrogenation is preferable to that of alkenes under some conditions. The overall reaction is shown in Eq. (1):

\[
\text{R} \xrightarrow{\text{H₂}} + \text{CO₂} + 2\text{H₂} \rightarrow \text{R}-\text{CHO} + \text{H₂O} + \text{H₂} \rightarrow \text{R}-\text{OH}.
\]

2. Results and discussion

Typical results are summarized in Table 1. In the presence of LiCl, H₄Ru₄(CO)₁₂, a tetranuclear ruthenium complex, effectively catalyzes the hydroformylation of cyclohexene with CO₂. At 140°C, hydroxymethylcyclohexane, the hydrogenated product of formylcyclohexane, is formed with a yield of 88% (Entry 1), which is almost comparable to the result of hydroformylation with CO using the same catalyst system (Entry 2). Among the additive salts tested, LiCl is the most efficient catalyst for the hydroformylation with CO₂.
(Entries 1, 3–6), but in the absence of salts, only the hydrogenation of cyclohexene proceeds (Entry 7). It is convenient to use Ru₃(CO)₁₂ as a catalyst precursor (Entry 8), which is transformed into tetranuclear complexes during the reaction [3]. On the other hand, phosphine complexes such as RuCl₂(PPh₃)₃ are not effective for this reaction (Entry 9). Terminal alkenes also undergo the hydroformylation to give the corresponding aldehydes and alcohols (Entries 10, 11); however, the yields and selectivities are not so high as with cyclohexene.

Fig. 1 shows the effects of reaction temperature on the hydroformylation of cyclohexene. The formation of formylcyclohexane can be observed even at a temperature as low as 80°C. Its yield reaches 50% at 120°C and rapidly decreases over this temperature. Instead, the yield of alcohol becomes significant at this temperature and reaches as high as 88% around 140°C. Even at higher temperatures, the hydrogenation of cyclohexene, an undesirable side reaction, is much less significant than hydroformylation.

There are two possible pathways for the synthesis of aldehyde from alkene, CO₂ and H₂ (Scheme 1); one is based on the hydroformylation of alkene with the CO formed by the hydrogenation of CO₂ (Path A), and the other depends on the hydrocarboxylation of alkene with CO₂ (Path B). Concerning reaction path B, some alkenes coordinated to complexes are known to react stoichiometrically with CO₂ to give five-membered metallacyclic complexes [5–7]. However, the contribution of this path appears to be very little since no formation of cyclohexanecarboxylic acid is observed even at low temperatures.

On the other hand, the reaction path A is supported by the effect of anions (Entries 1, 5, 6); the
yield of hydroformylation increases in the order of Cl\textsuperscript{−} > Br\textsuperscript{−} > I\textsuperscript{−}, which is consistent with that observed in the hydrogenation of CO\textsubscript{2} to CO\textsuperscript{3}. Besides, the reaction solution of Entry 1 exhibits strong IR bands in the CO region at 2037, 2016, 1998, 1987, and 1952 cm\textsuperscript{−1}, which can be attributed to the mixture of [H\textsubscript{3}Ru\textsubscript{4}(CO)\textsubscript{12}]\textsuperscript{−} [8] and [HRu\textsubscript{3}(CO)\textsubscript{11}]\textsuperscript{−} [9]. The former tetranuclear complex is known to be an active species for the hydrogenation of CO\textsubscript{2} to CO [3], while the latter trinuclear complex is one for the hydroformylation of alkene with CO [10]. This trinuclear complex is considered to be formed from the tetranuclear complex and CO formed in the reaction as shown in Eq. (2) [11].

\[
\frac{3}{4}[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^- + 2\text{CO} \rightleftharpoons [\text{HRu}_3(\text{CO})_{11}]^- + \frac{5}{4}\text{H}_2
\]  

Additional studies directed towards improving the efficiency on the terminal alkenes are underway.

3. Experimental

Typical experiment: cyclohexene (5.0 mmol), H\textsubscript{4}Ru\textsubscript{4}(CO)\textsubscript{12} (0.1 mmol) [12], and LiCl (0.4 mmol) were dissolved in 8.0 ml of N-methyl-2-pyrrolidone (NMP) in a 50-ml stainless-steel autoclave. After being pressurized with CO\textsubscript{2} (4.0 MPa) and H\textsubscript{2} (4.0 MPa), it was heated at 140°C for 30 h. After cooling to room temperature, the resulting gas and solution were analyzed by GC and GC-MS. The reaction solution was clear red-brown and no precipitate was observed. The products were 8.7 mmol of CO, 4.4 mmol (88% based on cyclohexene) of hydroxymethylcyclohexane, 0.1 mmol (2%) of formylcyclohexane, and 0.3 mmol (6%) of cyclohexane.

References