# Biphasic Hydroformylation of 1-Hexene with Carbon Dioxide Catalyzed by Ruthenium Complex in Ionic Liquids

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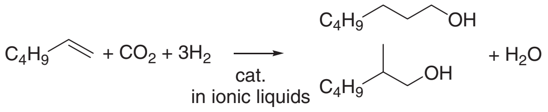
(Received October 7, 2003; CL-030949)

Hydroformylation of 1-hexene using carbon dioxide as carbonyl carbon source attained high yield and good chemoselectivity in heptanols when a ruthenium complex was used in biphasic ionic liquid–toluene system.

Carbon monoxide (CO) is one of the most useful raw chemical materials for the production of hydrocarbons, aldehydes, alcohols, and organic acids on an industrial scale, but with a major disadvantage of high toxicity. In contrast, carbon dioxide ($CO_2$) is an ideal raw material, because it is safe, abundant, and inexpensive. In our attempts to use $CO_2$ as a substitute for CO,[1–6] we recently reported a novel hydroformylation using $CO_2$ as carbonyl carbon source in the presence of ruthenium complex and halide salts catalyst system.[6] This catalysis was effectively performed with several alkenes to give corresponding alcohols in good yields. However, some problems remained unsolved with this catalytic system; alkene hydrogenation proceeded prior to hydroformylation with terminal alkenes; effective solvents such as *N*-methyl-2-pyrolidone (NMP) were with so high boiling points that it might cause some difficulties of separating the products from the solvent by distillation, when it would be put into industrial practice.

In view of those situations, we have taken up ionic liquids, on which much attention has been focused as a new reaction media in recent years. One of the attractive characters of ionic liquids is immiscibility with a number of organic solvents, enabling their use as a nonaqueous alternative solvent in two-phase systems.[7,8] The catalyses using two-phase system have been known to have advantages that products can be separate from a catalyst phase by simple extraction and that it is possible to modulate the reaction selectivity. Here we report an improved hydroformylation of 1-hexene with $CO_2$ using ruthenium complex in a biphasic catalytic system consisting of ionic liquid and organic solvent (Eq 1).



(1)

**Table 1.** Hydroformylation of 1-hexene with $CO_2$ catalyzed by a ruthenium complex in ionic liquids[a]

| Entry | Ionic liquid | Co-solv. | Conv. /% | Yield/%[b] Alcohol | Aldehyde | Alkane |
|---|---|---|---|---|---|---|
| 1 | [bmim]Cl | toluene | 97 | 84 | 0 | 11 |
| 2[c] | – | NMP | 98 | 64 | 5 | 24 |
| 3[d] | [bmim]Cl | toluene | 96 | 82 | 0 | 12 |
| 4[e] | [bmim]Cl | toluene | 78 | 60 | 0 | 14 |
| 5 | [bmim]Cl | $C_6H_{12}$ | 37 | 20 | 0 | 13 |
| 6 | [bmim]Cl | $Et_2O$ | 78 | 66 | 0 | 8 |
| 7 | [bmim]Cl | THF | 88 | 79 | 0 | 9 |
| 8 | [emim]Cl | toluene | 76 | 60 | 0 | 12 |
| 9 | [omim]Cl | toluene | 98 | 80 | 0 | 16 |
| 10[c] | [bmim]$BF_4$ | toluene | 96 | 63 | 0 | 26 |
| 11[c] | [bmim]$PF_6$ | toluene | 95 | 3 | 0 | 86 |
| 12 | [bmpy]Cl | toluene | 98 | 65 | 0 | 10 |

[a]The reaction was performed as described in Ref. 9. [b]Based on 1-hexene. [c][PPN]Cl (0.4 mmol) was added. [d]The second run. [e]The fourth run.

Hydroformylation with $CO_2$ proceeds in two steps: $CO_2$ is converted initially into CO, which in turn becomes the reagent of hydroformylation of the substrate.[6] For the first conversion of $CO_2$ to CO, the key process is deprotonation of a ruthenium hydride complex with halide anions to form an active species that coordinates to $CO_2$.[3] Among the halide anions examined as an additive, chloride salts are the most effective ones because of their high proton affinity.[3,6] On the basis of those findings, we chose 1,3-dialkylimidazolium chloride salts as ionic liquids. Although most of them are solid at room temperature, they melt at around 100 °C or below. Some representative results are summarized in Table 1.[9] In the toluene/[bmim]Cl system (bmim = 1-*n*-butyl-3-methylimidazolium), the reaction proceeded smoothly to give a mixture of C7 alcohols in 84% yield (Entry 1), while the yield of these alcohols remained 64% and the corresponding aldehydes were also formed with NMP (Entry 2). Unfortunately, the regioselectivity was not improved by using ionic liquid; both reaction systems gave mixtures of almost equimolar amounts of *n*-heptanol and 2-methylhexanol. Once the reaction reached completion, the mixture was spontaneously separated into organic and ionic liquid layers. Although the produced alcohols were present in both layers, they could be easily extracted using diethyl ether. The remaining mixture of ruthenium complexes and [bmim]Cl could be reused with almost the same activity for the second run (Entry 3), while its catalytic activity was considerably decreased by the fourth run, probably due to the accumulation of water that suppressed the CO formation (Entry 4).

It is necessary that organic co-solvent should be miscible with ionic liquid under the reaction conditions so that the substrate alkenes could contact with catalysts present in ionic liquid phase. Many factors are related to the miscibility of organic compounds with ionic liquids.[10] In general, the miscibility increases in the order of polarity of organic compounds but it also depends on their aromaticity, because aromatic compounds have CH$\cdots\pi$ or $\pi$–$\pi$ interaction with ionic liquids resulting in their relatively high miscibility. The conversion of 1-hexene was thus affected by the miscibility of the co-solvents with [bmim]Cl and increased in the order of cyclohexane < $Et_2O$ < THF < toluene (Entries 1, 5–7).

Another important factor affecting the alkene reactivity is the lipophilicity of imidazolium cations that increases with increased alkyl chain length. Thus, the conversion of alkene was relatively low in the reaction with [emim]Cl (emim = 1-ethyl-3-methylimidazolium) due to its less miscibility (Entry 8). On the other hand, a more miscible salt, [omim]Cl (omim = 1-*n*-octyl-3-methylimidazolium), afforded a single phase, which seemed responsible for the decreased chemoselectivity (Entry 9).

Ionic liquids with anions other than chloride were much less effective; even in the presence of a small amount of a chloride salt, the hydroformylation in [bmim]$BF_4$ gave lower yield and chemoselectivity in alcohols (Entry 10). In [bmim]$PF_6$, a degradation of the catalyst was observed as an unknown yellow complex precipitated, resulting in only a slight formation of hydroformylation products (Entry 11). A pyridinium chloride (bmpy = 1-*n*-butyl-4-methylpyridinium) gave a considerable amount of hydroformylation products, but unfortunately degraded as the alcohols were produced (Entry 12).

In conclusion, 1,3-dialkylimidazolium chlorides can make a useful media for hydroformylation with $CO_2$. They provide biphasic systems and high concentration in chloride anion, which may be the cause of the improved chemoselectivity in favor of hydroformylation. Moreover, the extraction of products and the recycling of catalysts become much easier compared with the conventional method. Further investigation is in progress to improve the catalyst recycling.

This study was supported by Industrial Technology Research Grant Program in ’02 from NEDO of Japan.

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9 In a typical experiment, a solution of $Ru_3(CO)_{12}$ (0.1 mmol), [bmim]Cl (1.0 g), and 1-hexene (5.0 mmol) in toluene (5.0 mL) was placed in a 50-mL stainless-steel autoclave. $CO_2$ (4.0 MPa) and $H_2$ (4.0 MPa) were introduced at room temperature and then the reactor was heated to 140 °C and held at that temperature for 30 h with stirring. After the reaction was completed, the resulting reaction mixture was separated into a toluene phase and an ionic-liquid phase. GC analysis indicated that the former contained 2.7 mmol of C7 alcohols, 0.6 mmol of hexane and 0.1 mmol of 1-hexene and the latter contained 1.5 mmol of C7 alcohols. The total yield of C7 alcohols was 84%. After evaporating the volatiles and then extracting the ionic liquid several times with diethyl ether, the crude mixture of C7 alcohols was recovered. This mixture was then purified by Kugelrohr distillation (isolated yield = 80%).

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