C−H Bond Activation in Dense Carbon Dioxide: Rhodium-Catalyzed Methane Carbonylation and Alkane Dehydrogenation

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The direct and selective functionalization of alkanes under mild conditions is one of the key issues for synthetic chemists.[1] A major problem in C−H bond activation by molecular catalysis is the lack of suitable solvents because most organic solvents are not tolerant under alkane activation conditions and prevent the desired reactions. Several compounds have been proposed for solving this problem, such as liquid xenon,[2] perfluoro organics,[3] and bulky hydrocarbons.[4] However, more inexpensive reaction media with adequate solubility for both the catalysts and alkanes are strongly desired. On the other hand, dense carbon dioxide has recently attracted increasing attention as an efficient and environmentally friendly reaction medium.[5] In the present paper, we report the methane carbonylation and alkane dehydrogenation by molecular catalysis in dense carbon dioxide. Although ruthenium-catalyzed alkane conversion in supercritical carbon dioxide was attempted recently, no C−H bond activation was observed.[6]

The production of fundamental chemicals based on methane is of great importance in view of so-called "green chemistry" because methane is a typical sustainable resource.[7] We have been investigating the direct carbonylation and dehydrogenation of alkanes catalyzed by the $RhCl(L)(PMe_3)_2-h\nu$ system (L = two electron-donor ligands).[8] In these reactions, the alkane itself was used as a reaction medium to dissolve the substrates and the catalyst. However, this methodology is hard to apply to methane transformation due to the low boiling point of methane. In this context, dense carbon dioxide seems very promising as a reaction medium because it is miscible with gaseous compounds such as methane and possibly stable enough to survive under alkane activation conditions. Hence, we examined the carbonylation of methane in carbon dioxide (eq 1).

Table 1. Carbonylation of Methane in Dense CO_2[a]

entry	catalyst	yield of CH_3CHO (turnover)
1	$RhCl(CO)(PMe_3)_2$	7.7
2	$RhCl(CO)(PRf_3)_2$[b]	27.9
3	$RhCl(PMe_3)_3$	21.5
4	$RhCl(PMe_3)_3$[c]	77.4
5	$RhCl(PMe_3)_3$[d]	9.4
6	$RhCl(PMe_3)_3$	12.2[e]

[a] Reaction conditions: Rh complex 0.014 mmol, methane 110 atm (89 mmol), CO 3 atm, CO_2 total pressure 300 atm, 4 °C, 16 h, irradiated with a 250 W high-pressure mercury lamp. [b] R_f: $CH_2CH_2(CF_2)_5CF_3$. [c] Benzaldehyde (18 μL) was added. [d] Reaction at 50 °C. [e] Yield of benzaldehyde: 89 mmol of benzene was used in place of methane.

$$CH_4 + CO \xrightarrow[\text{dense } CO_2]{\text{cat. Rh, } h\nu} CH_3CHO \qquad (1)$$

A typical experiment was carried out as follows. An autoclave with sapphire windows (20 cm^3 inner volume) was filled with a rhodium complex (0.014 mmol), carbon monoxide (3 atm), methane (110 atm), and carbon dioxide (up to 300 atm total pressure) at 4 °C. The reaction mixture was then irradiated for 16 h with a 250 W high-pressure mercury lamp (USHIO SP3-250). The reaction products were analyzed by GC using a capillary column, and all the volatile products were also characterized by GC−MS.

The results are summarized in Table 1. We first investigated the reaction using $RhCl(CO)(PMe_3)_2$ as a catalyst. Methane was carbonylated to afford acetaldehyde as expected (Table 1, entry 1); carbon dioxide did not disturb the C−H bond activation. In addition, acetic acid was not detected. To the best of our knowledge, this is the first successful example of the catalytic acetaldehyde synthesis from methane and carbon monoxide.[9] On the basis of the previous papers about the mechanism of the $RhCl(L)(PMe_3)_2-h\nu$ system in organic media,[10] the carbonylation of methane in dense carbon dioxide presumably proceeds via the oxidative addition of C−H bonds to $RhCl(L)(PMe_3)_2$ (Scheme 1).[11] The resulting

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[9] Stoichiometric formation of acetaldehyde from methane and CO under extremely high pressure was reported by a Russsian group. Enikolopyan, N. S.; Menchikova, G. N.; Grigoryan, E. A. *Dokl. Akad. Nauk SSSR* **1986**, *291*, 110−113.

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[11] We have found that the reaction of $RhCl(PMe_3)_3$ with benzene under irradiation gives the C−H bond addition product, $(C_6H_5)(H)RhCl(PMe_3)_3$. The details will be reported separately.

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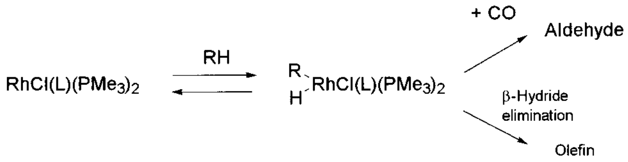
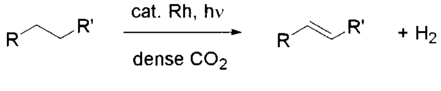
Scheme 1



methylrhodium complex will undergo CO insertion and reductive elimination to afford acetaldehyde.

The catalytic activity of $RhCl(CO)(PMe_3)_2$ was not very high probably due to the insufficient solubility in the methane−CO_2 mixture. Indeed, the use of a perfluorophosphine ligand resulted in a completely homogeneous reaction mixture and produced a higher yield (Table 1, entry 2). The Wilkinson-type complex, $RhCl(PMe_3)_3$, was also significantly soluble in the methane−CO_2 mixture to achieve a higher catalytic activity compared with $RhCl(CO)(PMe_3)_2$ (Table 1, entry 3). The addition of a small amount of benzaldehyde (18 μL) was quite effective for promoting the reaction (Table 1, entry 4). Acetaldehyde was obtained in 44% yield based on carbon monoxide. A possible explanation for this promoting effect is the participation of a radical mechanism via the photoactivation of benzaldehyde.[12] Another factor to control the catalytic activity may be the solubility of the rhodium species. Indeed, the addition of benzaldehyde kept the reaction mixture homogeneous throughout the reaction, while rhodium complexes were deposited out during the reaction in the absence of benzaldehyde. On the other hand, the higher reaction temperature led to the lower yield (Table 1, entry 5).[8b,13] It is also noteworthy that the carbonylation of methane takes place with a turnover comparable to that of benzene (Table 1, entries 3 and 6). Hence, we can conclude that molecular catalysis in dense carbon dioxide is a powerful tool for alkane transformation.

Since it was disclosed that dense carbon dioxide is promising as a reaction medium for the alkane carbonylation, we next investigated the dehydrogenation of cyclooctane in cyclooctane−CO_2 mixture catalyzed by the $RhCl(L)(PMe_3)_2-h\nu$ system (eq 2).[8a,c,d] The dehydrogenation also proceeds via the oxidative addition of C−H bond (Scheme 1). Experiments in dense carbon dioxide were carried out in a similar manner described for the methane carbonylation and were compared with the reactions in neat cyclooctane. These results are shown in Table 2. In all the cases, the catalysts were soluble in the reaction mixtures.



(2)

Table 2. Dehydrogenation of Cyclooctane in Dense CO_2[a]

entry	catalyst precursor	reaction media	yield of cyclooctene (turnover)
1	$[RhCl(PMe_3)_2]_2$	cyclooctane	23
2	$[RhCl(PMe_3)_2]_2$	cyclooctane + CO_2	322
3	$RhCl(PMe_3)_3$	cyclooctane	58
4	$RhCl(PMe_3)_3$	cyclooctane + CO_2	602

[a] Reaction conditions: Rh complex 0.014 mmol/Rh, cyclooctane (148 mmol) for entries 1 and 3, cyclooctane (74 mmol) and CO_2 150 atm for entries 2 and 4, 50 °C, 48 h, irradiated with a 250 W high-pressure mercury lamp.

$[RhCl(PMe_3)_2]_2$, an equivalent of the 14-electron species,[14] was not a very active catalyst in neat cyclooctane (Table 2, entry 1). In contrast, the reaction in the cyclooctane−CO_2 mixture proceeded much more efficiently (Table 2, entry 2). It is noteworthy that nearly the theoretical amount of hydrogen was detected in the reaction mixture and the formation of formic acid was negligible. Similarly, the dehydrogenation using $RhCl(PMe_3)_3$ proceeded smoothly in the cyclooctane-CO_2 mixture (entries 3 and 4). The yield of cyclooctene reached 11.4% based on the starting cyclooctane.

As for the reactions under CO_2 pressure, CO_2 complexes such as $RhCl(CO_2)(PMe_3)_2$ would be involved. However, in the dark, we have not yet succeeded in observing such an indication in ^{31}P NMR spectra of $[RhCl(PR_3)_2]_2$ or $RhCl(PR_3)_3$ up to 60 atm of CO_2[15] and in high-pressure IR spectra up to 50 atm.[16] To investigate the complex structure after the photocatalysis, the reaction mixture was evaporated, and the residue was analyzed by ^{31}P NMR in C_6D_6. The major species was assigned to $RhCl(CO)(PMe_3)_2$ along with a small amount of trimethylphosphine oxide.[17] Hence, the acceleration effect in the cyclooctane−CO_2 mixture is at least partly ascribed to the change in the complex structure.

In summary, we have revealed that dense carbon dioxide is an efficient reaction medium for C−H bond activation by molecular catalysis. Please note that carbon dioxide has many advantages over previously proposed reaction media. It is nontoxic, nonflammable, abundant, inexpensive, highly miscible with hydrocarbons, and easily separated from the reaction mixture. We are currently eager to apply this methodology to various alkane transformations.

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(17) $[RhCl(PMe_3)_2]_2$ was converted to $RhCl(CO)(PMe_3)_2$ in 33% yield after the reaction based on the UV and ^{31}P NMR spectra. No rhodium species other than $RhCl(CO)(PMe_3)_2$ were observed.