Palladium(II)-catalyzed oxidation of acrylate esters to acetals in supercritical carbon dioxide

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The development of a new palladium(II)-catalyzed oxidation of methyl acrylate, affording methyl 3,3-dimethoxypropanoate in excellent conversion and selectivity in supercritical CO_2, is presented.

Alkyl 3,3-dialkoxypropanoates are important intermediates in organic synthesis and have been used to synthesize a variety of compounds, including coumarins,[1] porphyrins,[2] spermine metabolites[3] and loganin.[4] Previously reported methods for the preparation of alkyl 3,3-dialkoxypropanoates are not satisfactory, due to the high cost of the starting materials and the low overall yields of the process. The Pd^{II}-catalyzed oxidation of terminal olefins with water, which is well known as the Wacker reaction, produces methyl ketones.[5] A similar reaction of terminal olefins bearing electron-withdrawing groups upon treatment of alcohols catalyzed by Pd^{II} affords acetals at the terminal carbon in DME. High yields of methyl 3,3-dimethoxypropanoate (92%), however, were afforded only in the presence of HMPA. In the absence of HMPA the yield was only 46%.[6]

Using supercritical carbon dioxide ($scCO_2$) as a reaction solvent has been attracting extensive attention in recent years. First, CO_2 is inexpensive, nonflammable, nontoxic[7] and chemically inert under many conditions. $ScCO_2$, as an environmentally friendly reaction medium, may be a substitute for volatile and toxic organic solvents.[8] Secondly, $scCO_2$ possesses hybrid properties of both liquid and gas, to the advantage of some reactions involving gaseous reagents.[9] Control of the solvent density by variation of the temperature and pressure enables the solvent properties to be 'tuned' to reactants.[10] Finally, separating of CO_2 from the reaction mixture is energy-efficient and simple.

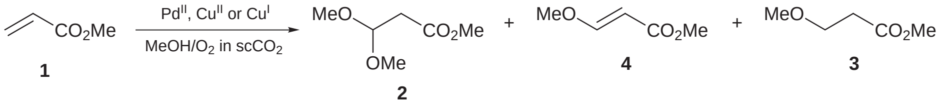
Organic reactions in $scCO_2$ have facilitated great progress in organometallic chemistry, particularly in homogeneous and heterogeneous catalysis. Several recent reports have shown that some interesting results are specifically associated with the use of $scCO_2$ as a reaction solvent.[11] Here we disclose our work on a Pd^{II}-catalyzed terminal olefin oxidation in $scCO_2$.‡ Our results show that Pd^{II}-catalyzed oxidation of methyl acrylate could be successfully processed in $scCO_2$ to give the dimethyl acetal as major product when an excess of MeOH was used (Scheme 1). Our previous experiments show that it is necessary to add an excess of MeOH to promote partial dissolution of the inorganic catalysts in $scCO_2$, since MeOH is miscible in $scCO_2$.[12]

The catalytic activity of $PdCl_2$ and $PdCl_2(MeCN)_2$ for oxidation of methyl acrylate were investigated. The reaction catalyzed by $PdCl_2$ were slightly faster than that by $PdCl_2(MeCN)_2$ (Table 1, entries 2 and 3).

It has been reported that CuCl was superior to $CuCl_2$ as the cocatalyst in the oxidation of acrylate esters.[13,6b] Interestingly, in our experiments carried out in $scCO_2$, 0.4 equiv. of $CuCl_2$ gave similar or even better results than the same amount of CuCl (Table 1, entries 8 and 9).

Hosokawa reported that the oxidation of methyl acrylate to the acetal was carried out at 50 °C in DME.[6] We found that the oxidation reaction could be completed at a lower temperature in $scCO_2$. In our experiment, the reaction afforded very good conversion and selectivity at 40 °C. The reaction was still smoothly accomplished at 27 °C, at which temperature CO_2 is a liquid, although the amount of byproducts increased slightly.

The CO_2 pressure had a great effect on the selectivity. The best results were obtained when the pressure of CO_2 was controlled between 12–13 MPa. As the pressure of CO_2 was reduced, the conversion and selectivity also declined. For example, the reaction gave **2** in a yield of only 75.8% and the



Scheme 1

Table 1 Oxidation reaction of methyl acrylate in $scCO_2$[a]

Entry	Catalyst	T/°C	P_{O_2}/MPa	P_{CO_2}/MPa	Conv.	Yield[b] (%) **2**	**3**	**4**	Selectivity for **2**[c] (%)
1	$PdCl_2(MeCN)_2$, CuCl[d]	50	0.1	13	99.0	81.1	3.5	8.8	86.8
2	$PdCl_2(MeCN)_2$, CuCl[d]	50	0.1	13	49.4	36.6	5.9	2.7	81.0
3	$PdCl_2$, $CuCl_2$[e]	50	0.1	13	71.0	42.9	6.6	3.1	81.6
4	$PdCl_2$, $CuCl_2$	50	0.1	13	98.5	82.7	4.0	3.5	91.7
5	$PdCl_2(MeCN)_2$, CuCl	40	0.1	12	93.0	82.4	2.8	3.0	93.4
6	$PdCl_2$, $CuCl_2$	27	0.1	12	93.0	75.0	5.1	2.9	90.3
7	$PdCl_2$, $CuCl_2$	40	0.1	9	92.0	75.8	2.8	3.4	92.4
8	$PdCl_2$, $CuCl_2$	40	0.5	13	99.1	87.9	1.6	2.5	95.5
9	$PdCl_2$, CuCl	40	0.5	13	99.7	86.3	1.5	4.5	93.5
10	$PdCl_2$, $CuCl_2$	40	1.0	12	99.4	91.7	1.2	2.0	96.6

[a] Methyl acrylate (5 mmol), MeOH (1 ml ≈ 24.7 mmol), $PdCl_2$ or $PdCl_2(MeCN)_2$ (3 mol%), CuCl or $CuCl_2$ (0.4 equiv.), 12 h. [b] By GC. [c] Selectivity = [**2**/(**2** + **3** + **4**)] × 100. [d] $PdCl_2(MeCN)_2$ (1 mol%), CuCl or $CuCl_2$ (2 mol%). [e] $CuCl_2$ (2 mol%).

amount of other unidentified products increased when 9 MPa CO_2 was charged in the autoclave.

The oxygen pressure also affected the conversion and selectivity. Lower oxygen pressure (0.1 MPa) gave satisfactory conversion but the selectivity to **2** was never higher than 93.4%. The best selectivity (over 96%) was obtained as the oxygen pressure was elevated to 1.0 MPa. Using ethyl acrylate as the substrate, the reaction affords similar results, and the further experiments are now in progress.

In summary, the oxidation reaction of methyl acrylate afforded the acetal in high conversion and selectivity at lower temperature when supercritical carbon dioxide instead of DME was used as the reaction medium without the presence of HMPA. The pressure of CO_2 and O_2 had a remarkable effect on the conversion and selectivity.

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Notes and references

† Typical procedure: Reactions were carried out in a HF-25 autoclave. Pd^{II} catalyst (0.15 mmol, 3 mol%), $CuCl_2$ (4 mmol), MeOH (1 ml, 24.7 mmol) and acrylate ester (5 mmol) were added into a 25 ml autoclave in sequence. O_2 and then liquid CO_2 were pumped into the autoclave using a cooling pump to give the desired pressure. The autoclave was then put into an oil bath under magnetic stirring for the desired reaction time. After the reaction, the autoclave was allowed to cool to −30 °C. CO_2 was vented and the surplus was extracted with n-hexane. The extract was filtrated and condensed under reduced pressure. The product was analyzed using GC (quantitative analysis) and GC-MS, ^1H NMR ^{13}C NMR and IR analysis (identification of products).

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