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Rapid hydroformylation of alkyl acrylates in supercritical CO_2

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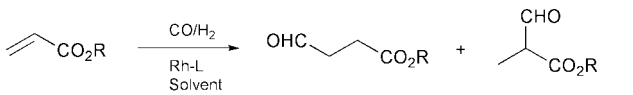
Fast and regioselective hydroformylation of alkyl acrylates can readily be accomplished in supercritical CO_2 ($scCO_2$), which promotes the reaction probably *via* specific solvent–solute interactions.

The hydroformylation of acrylic esters produces bifunctional compounds, which can be converted into synthetically useful intermediates such as malonic acid and 1,4-dicarboxylic acid derivatives and butyrolactones. In the past three decades or so, a number of publications have appeared, directed towards effecting the reaction with acceptable rates and regioselectivities.[1–10] In this context, catalysts based on various rhodium-ligand combinations have been examined. However, in common organic solvents and regardless of the ligands that have been tested, the reaction is in general slow and high temperature and/or high pressure are often required.[1,6,7,9,10] For example, in the hydroformylation of ethyl acrylate in ethylbenzene, complete conversion, corresponding to an average turnover frequency (TOF) of 413 h^{-1}, of the olefin was only achieved in 5 h reaction time at 150 °C and *ca.* 100 bar syngas using $[RhCl(CO)_2]_2$ in the presence of bis(diphenylphosphino)butane (DPPB).[1] While milder reaction conditions are possible with phosphite[4] and phosphanobornadiene ligands,[2] the TOFs were very low. Much improved rates have recently been obtained when the reaction is run under organo-aquo biphasic conditions or when a 'supported aqueous phase' catalyst is used.[5,8] However, low solubilities of the less hydrophilic acrylates in water limit the applicability of the biphasic systems and, in the case of the latter, it was shown that even a slight alteration in the water content in the supported aqueous phase could sharply reduce the activity of the catalyst. We report herein that fast and selective hydroformylation of alkyl acrylates can readily be effected in $scCO_2$ in the presence of $[Rh(acac)(CO)_2]$ and the fluoroalkylated phosphine ligand $P(p\text{-}C_6H_4C_6F_{13})_3$ (Scheme 1).[11]

We first tested this ligand in the hydroformylation of butyl acrylate in toluene and compared the results obtained with three other ligands, PPh_3, DPPB and $P(p\text{-}C_6H_4OMe)_3$, of which the first two are frequently used and DPPB is one of the most effective ligands in liquid solvents.[1,5,7] The reaction was performed using a combination of $[Rh(acac)(CO)_2]$ and 10 equiv. of a phosphine ligand as catalyst precursor in an autoclave at 80 °C and 20 bar H_2–CO (1:1) with the initial olefin concentration being 0.28 M. All the reactions were run for 1 h and were homogeneous throughout. The results are summarized in Table 1. Consistent with previous findings, DPPB stands out as the most effective ligand in terms of the average TOF to aldehydes given in Table 1. With PPh_3 and the relatively electron-rich $P(p\text{-}C_6H_4OMe)_3$, the expected aldehydes could barely be detected. With the electron-deficient $P(p\text{-}C_6H_4C_6F_{13})_3$, a TOF of 85 was observed. Increasing the syngas pressure to 50 bar led to some increase in TOF to 122, which is still significantly lower than the value of 304 with DPPB. Judging from these values, it is clear that hydroformylation of acrylates in normal organic solvents by arylphosphines, including the most effective DPPB, will be of little practical value.



$scCO_2$: TOF up to 1877
Toluene: TOF < 200

R = Me, Bu, ^{t}Bu
L = $P(p\text{-}C_6H_4C_6F_{13})_3$, $P(p\text{-}C_6H_4OMe)_3$, PPh_3, DPPB
Solvent = $scCO_2$, toluene

Scheme 1

Table 1 Hydroformylation of butyl acrylate by Rh-L in toluene[a]

L	Pressure/ bar	Conv. (%)[b]	Ald. (%)[c]	TOF/h^{-1}[d]
PPh_3	20	< 1		
$P(p\text{-}C_6H_4OMe)_3$	20	< 1		
$P(p\text{-}C_6H_4C_6F_{13})_3$	20	2.1	99.8	85
$P(p\text{-}C_6H_4C_6F_{13})_3$	50	2.7	99.8	122
DPPB	20	7.6	99.9	304

[a] Reactions were carried out at L–$[Rh(acac)(CO)_2]$ = 10, olefin–rhodium = 4000, olefin concentration = 0.28 mol dm^{-3}, 80 °C and indicated H_2–CO (1:1) pressure in 20 mL of toluene for 1 h, with product analysed by GC. [b] Conversion of the acrylates. [c] Selectivity to branched aldehydes. The linear aldehydes were not detected by GC. The hydrogenated product, propionates, accounts for the product balance. [d] Average turnover frequency: mole of aldehyde formed per mole of catalyst per hour.

Having determined the activity of the Rh-$P(p\text{-}C_6H_4C_6F_{13})_3$ catalyst in toluene, we then applied the same catalyst to the hydroformylation of methyl, butyl and ^{t}butyl acrylates in $scCO_2$ (Scheme 1).† The reactions were carried out for 1 h and the detailed procedure has been described before.[11] Table 2 summarises the results obtained in $scCO_2$ and those in toluene under the same temperature, pressure and olefin concentrations. In all these reactions, the linear aldehydes could not be detected by GC, which is in line with the literature that the hydroformylation of acrylates usually affords branched aldehydes as the dominant product.[1–10] The ratio of the hydrogenated product, propionates, was somewhat higher in $scCO_2$ (*ca.* 2.5%) than in toluene (< 0.5%). However, of much more significant

Table 2 Hydroformylation of acrylates by Rh-$P(p\text{-}C_6H_4C_6F_{13})_3$ in $scCO_2$ and toluene[a]

Substrate	Solvent	[Olefin][b]	Conv. (%)[c]	Ald. (%)[d]	TOF/ h^{-1}[e]
Methyl acrylate	$scCO_2$	0.45	40.8	97.6	1593
Butyl acrylate	$scCO_2$	0.28	42.9	97.5	1671
^{t}Butyl acrylate	$scCO_2$	0.28	46.9	97.4	1827
Methyl acrylate	Toluene	0.45	2.3	99.6	92
Butyl acrylate	Toluene	0.28	2.1	99.8	84
^{t}Butyl acrylate	Toluene	0.28	4.8	99.6	191

[a] Reactions were carried out at $P(p\text{-}C_6H_4C_6F_{13})_3$–$[Rh(acac)(CO)_2]$ = 10, olefin–rhodium = 4000, 80 °C, 180 bar CO_2 and 20 bar H_2–CO (1:1) for 1 h. [b] Olefin concentration: mol dm^{-3}. [c] Conversion of the acrylates. [d] Selectivity to branched aldehydes. The linear aldehydes were not detected by GC. The hydrogenated product propionates accounts for the product balance. [e] Average turnover frequency.

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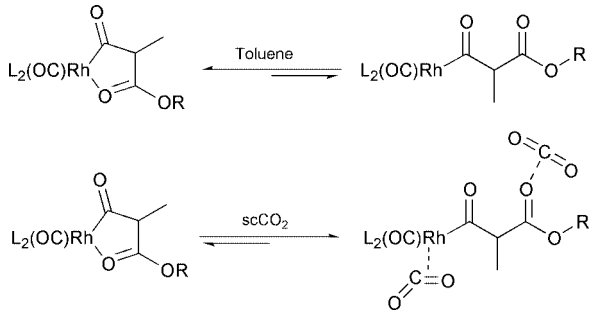

Scheme 2

interest is the observation that, in $scCO_2$, the average TOFs for the formation of aldehydes ranged from 1593 to 1827 h^{-1}, whereas in toluene the TOFs were less than 200 h^{-1}. In both solvents, the fastest rates were derived from the sterically most demanding ^{t}butyl acrylate. Thus, by simply changing the reaction medium from toluene to $scCO_2$, the TOF values increased *ca*. 10–20 fold. Such dramatic enhancement in reaction rates by $scCO_2$ has rarely been observed before,[11–14] although the high miscibility of various gases with CO_2 and its excellent transport properties have often been suggested to be impetus for fast reactions.[15] One of the best-known examples, where greatly improved rates were achieved, is the hydrogenation of CO_2 by a Ru-PMe_3 catalyst, the high rates being partly attributed to the high concentration of the gaseous reagents.[15] In the present study, the enhanced TOFs are less likely to be primarily due to a high concentration of syngas in $scCO_2$, since more than doubling the pressure for the hydroformylation of butyl acrylate in toluene led to a TOF of only 122 h^{-1} (Table 1), far less than that of 1671 h^{-1} obtained in $scCO_2$ at 20 bar.

A further demonstration of the rate enhancement aforesaid is the hydroformylation of a mixture of butyl acrylate and dec-1-ene in $scCO_2$. The reaction was run under identical conditions to those for butyl acrylate itself, except with the concentration of the olefin reduced by *ca*. half (0.12 M for both dec-1-ene and butyl acrylate). The TOFs observed for butyl acrylate and dec-1-ene were 1511 and 379 h^{-1}, respectively. This is remarkable, considering that in the absence of the acrylate the average TOF for dec-1-ene (0.22 M initial concentration) was 2794 h^{-1} under otherwise identical reaction conditions.[11] In a similar experiment in toluene, the TOF was found to be 56 for the acrylate and 24 h^{-1} for dec-1-ene, while in the absence of the acrylate the TOF for the latter olefin (0.28 M) rose to 901. Evidently, the Rh-P(*p*-$C_6H_4C_6F_{13})_3$ catalyst is considerably more chemoselective towards the less reactive acrylates, but it is only in $scCO_2$ where it becomes highly active as well.

The significant enhancement in hydroformylation rates for the acrylates in $scCO_2$ might be accounted for by specific solvent–solute interactions. The low rates observed in common organic solvents are generally believed to be a result of the formation of thermodynamically stable five or six-membered rings (Scheme 2, where only the intermediate leading to branched product is shown).[7,8] The rate determining step of the hydroformylation has therefore been suggested to be the dissociation of the chelated carbonyl species to give a coordinatively unsaturated intermediate that is active towards the oxidative addition of H_2.[8] We suggest that, in $scCO_2$, the equilibrium position is shifted in favour of the key unsaturated intermediate as a result of a carbonyl–CO_2 donor–acceptor interaction as shown in Scheme 2. Previous spectroscopic studies have already shown that carbonyl groups can act as Lewis bases and interact with CO_2 acting as a Lewis acid.[16] In addition, coordination of CO_2 to the rhodium atom of the unsaturated intermediate and other oxygen atoms is possible, which would further shift the equilibrium to the right.[17] A similar model involving H_2O and hydrogen bonding was earlier proposed to account for the increase in rates in the hydroformylation of acrylates in the presence of water.[5,8]

In summary, we have shown that the hydroformylation of alkyl acrylates, although sluggish in conventional organic solvents, can readily be effected in $scCO_2$. In such reactions, CO_2 acts not only as a solvent but may also function as an electron acceptor, interacting with and stabilizing key carbonyl intermediates and thus promoting the overall reaction. Such specific solvent–solute interactions have rarely been exploited in catalysis in $scCO_2$ but could provide a unique means for tuning chemical activity and selectivity in synthesis in $scCO_2$.

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Notes and references

† **CAUTION**: When working with high-pressure equipment, appropriate safety devices, including but not limited to pressure relief mechanisms and blast shields, should be used.

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