

# Fast and unprecedented chemoselective hydroformylation of acrylates with a fluoropolymer ligand in supercritical CO<sub>2</sub>

Yulai Hu, Weiping Chen, Anna M. Banet Osuna, Jon A. Iggo and Jianliang Xiao\*

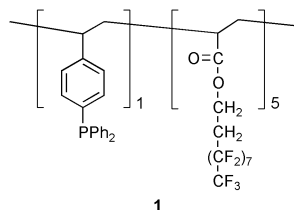
Leverhulme Centre for Innovative Catalysis, Department of Chemistry, University of Liverpool, Liverpool, UK L69 7ZD. E-mail: j.xiao@liv.ac.uk; Fax: (+44) 151 7943589; Tel: (+44) 151 7942979

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**A fluororous polymeric phosphine, when combined with supercritical CO<sub>2</sub> (scCO<sub>2</sub>) and rhodium, effects fast and highly chemoselective hydroformylation of acrylates, one of the least reactive olefins in hydroformylation reactions.**

Hydroformylation of acrylates produces synthetically valuable bifunctional compounds. Unfortunately, acrylates are one of the least reactive olefins towards H<sub>2</sub>-CO. Using [RhH(CO)(PPh<sub>3</sub>)<sub>3</sub>] as catalyst precursor, the hydroformylation rate of methyl acrylate was measured to be two orders of magnitude smaller than that of olefins such as alk-1-enes, allyl alcohol, and styrene.<sup>1</sup> Not surprisingly, in common organic solvents, the reaction is in general sluggish and high temperature and/or high pressure are often required, and although lots of studies have been carried out in the past three decades or so, few breakthroughs have been achieved.<sup>2</sup> We recently reported that when scCO<sub>2</sub> is used as reaction medium, rapid hydroformylation of alkyl acrylates can readily be effected by [Rh(acac)(CO)<sub>2</sub>] and a fluorinated ligand P(*p*-C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>F<sub>13</sub>)<sub>3</sub>.<sup>3</sup> We now report that the combination of the fluoropolymeric ligand **1**,<sup>4</sup> [Rh(acac)(CO)<sub>2</sub>], and the ecologically attractive scCO<sub>2</sub> brings about not only fast rates but unprecedented high chemoselectivity as well in the hydroformylation of these olefins. The incorporation of the fluorinated side chains in the polymer was expected to enhance the solubility of arylphosphines that are usually only sparsely soluble in scCO<sub>2</sub>, thus providing a simple way for performing catalysis with CO<sub>2</sub>-insoluble metal-phosphine complexes.<sup>5</sup>



We initially examined the hydroformylation of ethyl acrylate catalysed by [Rh(acac)(CO)<sub>2</sub>]-**1** under various conditions. Table 1 summarises the results obtained. Intriguingly, the average turnover frequency (TOF) for the formation of ethyl 2-formylpropionate varies with the pressure of CO<sub>2</sub>. Thus, the TOF was found to be 1255 h<sup>-1</sup> at 200 bar, but rose to a higher value of 2066 upon lowering the pressure to 150 bar. The change in rate with CO<sub>2</sub> pressure could be due to **1** adopting structures that vary with the density of CO<sub>2</sub> (*vide infra*), as has been shown for poly(vinyl acetate)-*block*-poly(fluoroacrylate) copolymers at higher CO<sub>2</sub> pressures.<sup>6</sup> Importantly, the combination of **1** and high pressure CO<sub>2</sub> proves to be essential for high rates. Thus, when the quantity of **1** was reduced by half while keeping the rhodium content constant, the TOF decreased from 2066 to 1251 and, in the absence of **1**, no aldehydes could be detected. At 120 bar total pressure, where liquid acrylate separated from CO<sub>2</sub>, significant polymerization of the acrylate resulted.<sup>7</sup> Furthermore, when carried out in liquid solvents such as toluene, hexane, and perfluoromethylcyclohexane, the latter two resembling scCO<sub>2</sub> in terms of solubility parameters,<sup>8</sup> the reaction was *ca.* 5 times slower. It should be pointed out that the

lower rates in the liquid solvents cannot be ascribed to interfacial mass transfer limitations; varying the agitation speed from 200 to 500 to 1100 rpm resulted in no significant variations in TOFs of the reaction in toluene (agitation speed ~ 900 rpm in Table 1). An additional demonstration of the effectiveness of the fluororous tags in conferring solubility on arylphosphines is seen in the same reaction in which PPh<sub>3</sub>, a ligand electronically similar to **1**, replaced **1** leading to a TOF of only 43. Consequently, our subsequent studies were carried out with **1** at a total pressure of 150 bar with a P:Rh ratio of 8. Using the conditions established, we extended the reaction to methyl, butyl, and *tert*-butyl acrylates. The results are given in Table 2. In line with the literature,<sup>2</sup> branched aldehydes dominated the products of these reactions, as can be seen from the high branched to linear aldehyde ratios (B:L). The ratio of the hydrogenated product, propionates, ranged between 1 to 2% and was lower than that observed with the molecular ligand P(*p*-C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>F<sub>13</sub>)<sub>3</sub>.<sup>3</sup> Remarkably, all the acrylates underwent the hydroformylation with TOF values greater than 2000. These values are far higher than those obtained in common organic solvents and represent one of the fastest rates reported so far for acrylate hydroformylation.

For instance, in the hydroformylation of ethyl acrylate in ethylbenzene,<sup>9</sup> complete conversion of the olefin, corresponding to a TOF value of 413 h<sup>-1</sup>, was only achieved in 5 h reaction

**Table 1** Hydroformylation of ethyl acrylate with Rh-**1** under various conditions<sup>a</sup>

Solvent	<i>P</i> bar <sup>b</sup>	P:Rh	Ald. (%) <sup>c</sup>	B:L <sup>d</sup>	TOF <sup>e</sup>
CO <sub>2</sub>	200	8	99.4	206	1255
CO <sub>2</sub>	150	8	99.0	155	2066
CO <sub>2</sub>	150	4	99.3	B <sup>f</sup>	1251
CO <sub>2</sub>	150	0	<sup>g</sup>		
CO <sub>2</sub>	120	8	<sup>h</sup>		
Hexane	30 <sup>i</sup>	8	99.5	B <sup>f</sup>	408
Toluene	30 <sup>i</sup>	8	99.7	B <sup>f</sup>	405
CF <sub>3</sub> C <sub>6</sub> F <sub>11</sub>	30 <sup>i</sup>	8	99.6	B <sup>f</sup>	440

<sup>a</sup> Reactions were performed at olefin concentration = 0.37 mol dm<sup>-3</sup> (assuming all the olefin to be dissolved), olefin to rhodium molar ratio = 6000, 30 bar H<sub>2</sub>-CO (1:1) and 80 °C for 1 h, with the product analysed by GC. <sup>b</sup> Total pressure. <sup>c</sup> Selectivity to aldehydes. The hydrogenation product ethyl propionate accounts for the product balance. <sup>d</sup> Branched to linear aldehyde molar ratio. <sup>e</sup> Average turnover frequency: mole of aldehydes formed per mole of catalyst per hour. <sup>f</sup> Linear aldehyde was not detected. <sup>g</sup> No reaction. <sup>h</sup> *ca.* 20% of the acrylate polymerised (<sup>1</sup>H NMR). <sup>i</sup> No CO<sub>2</sub>.

**Table 2** Hydroformylation of acrylates with Rh-**1** in scCO<sub>2</sub><sup>a</sup>

Substrate	[Olefin] <sup>b</sup>	Conv. (%) <sup>c</sup>	Ald. (%)	B:L	TOF
Methyl acrylate	0.45	38.2	98.4	155	2196
Ethyl acrylate	0.37	35.5	99.0	121	2066
Butyl acrylate	0.28	35.7	99.0	117	2081
<i>tert</i> -Butyl acrylate	0.28	35.6	99.2	111	2087

<sup>a</sup> See also Table 1. <sup>b</sup> Olefin concentration, mol dm<sup>-3</sup>. <sup>c</sup> Conversion of the acrylates.

time at 150 °C and *ca.* 100 bar syngas using  $[\text{RhCl}(\text{CO})_2]_2$  in the presence of bis(diphenylphosphino)butane, one of the best ligands known for this type of reaction.<sup>2</sup> In our previous study, several monodentate phosphines were examined for the hydroformylation of butyl acrylate in toluene, the best being  $\text{P}(p\text{-C}_6\text{H}_4\text{C}_6\text{F}_{13})_3$ , which afforded a TOF of 122 at 50 bar  $\text{H}_2\text{-CO}$  and 80 °C.<sup>3</sup> Much improved rates have recently been obtained when the reaction is run in the presence of water; but the rates are markedly affected even by a slight alteration in water content and by the solubility of acrylates in water.<sup>2b,d</sup>

Significantly more interesting is the observation that **1** is totally chemoselective towards acrylates. Under similar reaction conditions in  $\text{scCO}_2$ , dec-1-ene, hex-1-ene, styrene, and vinyl acetate all failed to react with  $\text{H}_2\text{-CO}$ . The only exception is allyl alcohol, which was converted to branched and linear aldehydes with a TOF of 118. This is remarkable, considering that all of these olefins have previously been shown to be much more reactive than methyl acrylate towards syngas in common solvents,<sup>1</sup> and alk-1-enes usually yield high TOF values in hydroformylations catalysed by soluble rhodium catalysts in  $\text{scCO}_2$ .<sup>10</sup> A further demonstration of the chemoselectivity of **1** is seen in the hydroformylation of an equimolar mixture of dec-1-ene and ethyl acrylate (olefin concentration = 0.14 mol  $\text{dm}^{-3}$ ) under conditions similar to those used for the pure acrylate (Scheme 1). A TOF of 872 was measured for ethyl acrylate converting into the branched aldehyde (B:L = 92). The lower TOF in comparison with that obtained with pure ethyl acrylate is likely to be a result of decreased olefin concentration. In stark contrast, no product arising from dec-1-ene could be detected by GC. A more striking example is the reaction of but-3-enyl acrylate. The C=C bond adjacent to the carbonyl group was hydroformylated to give but-3-enyl 2-formylpropionate with a TOF of 1525, while the remote C=C bond remained intact according to NMR and GC measurements.

It is generally believed that the low hydroformylation rates associated with acrylates in common organic solvents stem from the formation of thermodynamically stable five- or six-membered rings *via* the coordination of the acrylate carbonyl group to rhodium, with the reaction rate determined by opening of the ring to give a coordinatively unsaturated intermediate.<sup>2a,d</sup> The faster rates in  $\text{scCO}_2$  may result from  $\text{CO}_2$  facilitating the ring opening step by  $\text{CO}_2$ -carbonyl acid-base interactions and

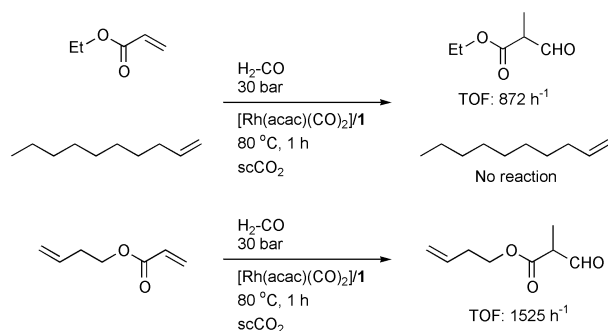
$\text{CO}_2$  coordination to rhodium.<sup>3,11</sup> The unique chemoselectivity of **1** in favour of acrylates over alk-1-enes could arise from a stronger acrylate binding to rhodium and be related to the structure of **1** in  $\text{scCO}_2$ . **1** contains  $\text{CO}_2$ -philic poly(fluoroacrylate) as well as  $\text{CO}_2$ -insoluble styryldiphenylphosphine segments, which can prompt the formation of aggregates or micellar structures in  $\text{scCO}_2$ ,<sup>6</sup> resulting in differential partitioning of olefins with differing polarities in and out of the catalyst-containing aggregates.<sup>12</sup>

To summarise, the results presented show that the combination of  $\text{scCO}_2$ , **1** and rhodium brings about not only excellent rates but also unique chemoselectivities in the hydroformylation of usually unreactive alkyl acrylates, suggesting that engineered macromolecular catalysts coupled with  $\text{scCO}_2$  could lead to novel activities and selectivities in reaction chemistry.

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**Scheme 1** Chemoselective hydroformylation of C=C bonds in  $\text{scCO}_2$