Reaction Activity and Selectivity as a Function of Solution Ionic Strength in Oct-1-ene Hydroformylation with Sulfonated Phosphines

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Salt concentration has a considerable influence on the activity and selectivity of water-soluble hydroformylation catalysts derived from $Rh(acac)(CO)_2$ and the sulfonated phosphine, $P[C_6H_4(CH_2)_3C_6H_4SO_3Na]_3$; addition of Na_2SO_4 or Na_2HPO_4 to the catalysts enhances the both the rate and selectivity of the hydroformylation reaction.

Considerable efforts have been directed towards the development of aqueous-phase hydroformylation catalysts with trisulfonated triphenylphosphine, TPPTS.[1-10] In almost all reported patent examples that show relatively high catalytic selectivity, either an ionic surfactant or a buffer component, *e.g.* Na_2HPO_4, is added to achieve better mixing of the two phases or to stabilize the pH.[7-10] Recently, we have demonstrated that the surface-active phosphines, $P[C_6H_4(CH_2)_xC_6H_4SO_3Na]_3$, ($x = 3, 6$), have improved reactivity and selectivity for the rhodium catalysed hydroformylation of oct-1-ene in aqueous methanol.[11] Here we report that salt concentration has considerable influence on oct-1-ene hydroformylation activity and selectivity with catalysts derived from $Rh(acac)(CO)_2$ and the sulfonated phosphine, $P[C_6H_4(CH_2)_3C_6H_4SO_3Na]_3$ when the reaction is performed in water.

The oct-1-ene hydroformylation system under investigation consists of an aqueous layer and an organic layer. In each case the aqueous layer was a 1.56 ml solution of $Rh(acac)(CO)_2$ (5 mmol dm^{-3}), and the corresponding amount of phosphine to give Rh/phosphine ratios of either 1 : 3, 1 : 10, or 1 : 20. The organic layer was a mixture of 0.6 ml oct-1-ene and 0.34 ml nonane (GC internal standard). The catalysis was done in a 30 ml stainless steel reactor equipped with a pressure gauge. The relatively large reactor volume ensured that only a small pressure drop occurred during the course of the reaction. The reactor was charged with $CO–H_2$ (1 : 1) to 14 atm after all the reactants were added; it was then placed in a preheated silicon oil-bath (120 °C). A constant stirring rate of 260 rpm was used in all reactions. All reactions were terminated after 24 h. The colourless organic layer was immediately analysed by gas chromatography.

The catalytic results, reaction activity as yield and selectivity as normal to branched nonanal ratio, with and without the added salts Na_2SO_4 and Na_2HPO_4 are given in Fig. 1. For comparison the results obtained with trisulfonated triphenyl phosphine are also given in Fig. 2.[12]

Addition of salt increases the ionic strength of aqueous solutions. Previous dynamic light scattering results demonstrate that the surface active phosphines, $P[C_6H_4(CH_2)_xC_6H_4SO_3Na]_3$ ($x = 3, 6$), aggregate in the presence of salt while TPPTS shows no evidence for aggregates of uniform size.[11] The results clearly show that the phosphine which can aggregate in aqueous salt solution, $x = 3$, leads to a more active hydroformylation catalyst compared to the catalyst prepared from TPPTS. Furthermore addition of salt to the catalysts derived from the surface-active phosphine improves the reaction rate while the rate drops significantly when salt is added to the TPPTS catalysts.

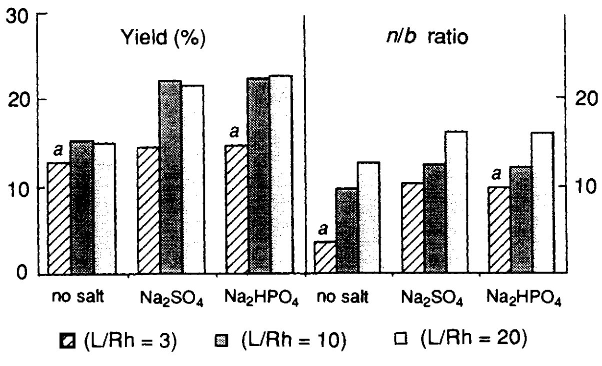

Fig. 1 The effect of salt on oct-1-ene hydroformylation with a surface active phosphine (^{a} data from ref. 12). Yields and selectivities for the hydroformylation of oct-1-ene with rhodium catalysts of $P[C_6H_4(CH_2)_3C_6H_4SO_3Na]_3$. The catalyst solutions were prepared from stock solutions of $Rh(acac)(CO)_2$ and $P[C_6H_4(CH_2)_3C_6H_4SO_3Na]_3$ in either water, 0.5 mol dm^{-3} Na_2SO_4, or 0.5 mol dm^{-3} Na_2HPO_4.

The solubility of oct-1-ene in water is expected to decrease as ionic strength increases. Hydroformylation of olefins with rhodium catalysts of sulfonated phosphines occurs in the aqueous phase,[13] thus the expected effect of added salt to aqueous solutions of hydroformylation catalysts is to reduce the reaction rate. While this is the observed behaviour of the TPPTS catalysts the opposite trend is observed with the surface active ligand. The rate enhancement with the phosphine, $x = 3$, is consistent with formation of micelles under the reaction conditions. It is suggested that the micelles serve to improve the water solubility of oct-1-ene.

Importantly as in the Rh/TPPTS system,[12] the Rh/$P[C_6H_4(CH_2)_3C_6H_4SO_3Na]_3$ catalysts also show significant enhancement of selectivity in the presence of salt. High ionic strength in the aqueous medium results in improved *n*/*b* ratios. Thus it is inferred that the salt concentration has an influence on the nature of the catalytic species in solution. It is generally accepted that a bis-phosphine rhodium intermediate leads to a higher proportion of the linear aldehyde in rhodium catalyzed hydroformylation reactions.[14] We suggest that high salt concentration increases the stability of bis-phosphine intermediates relative to mono-phosphine intermediates.[12] The rationale is that a rhodium complex of a sulfonated phosphine has the dimensions of a small micelle. Just as high ionic strength promotes the aggregation of surface active phosphines by stabilising the close proximity of many sulfonate groups at the surface of a micelle, high ionic strength should also stabilize the high net negative charge which results in the coordination sphere of a rhodium complex of sulfonated phosphines. It is further noted that the sulfonated ligands themselves are present as sodium salts, thus an increase in ligand/Rh ratio also leads to solutions of high ionic strength.

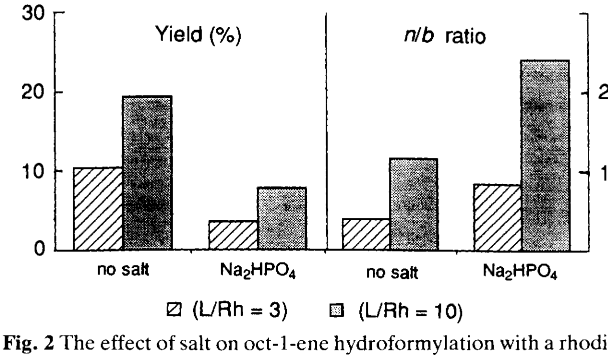

Fig. 2 The effect of salt on oct-1-ene hydroformylation with a rhodium catalysts of TPPTS. Yields and selectivities for the hydroformylation of oct-1-ene with rhodium catalysts of TPPTS. The catalyst solutions were prepared from stock solutions of $Rh(acac)(CO)_2$ and TPPTS in either water, or 0.5 mol dm^{-3} Na_2HPO_4.

The catalytic results show that surface-active phosphines in the hydroformylation of water-insoluble olefins have potential application in the development of water-bourne hydroformylation catalysts. This is a potentially environmentally benign alternative to cobalt based catalysts for the hydroformylation of higher olefins. Addition of salts to the catalytic system with surface-active phosphines enhances the rate of hydroformylation reaction, and at the same time gives excellent reaction selectivity.

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