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HYDROFORMYLATION OF OLEFINS WITH THE WATER SOLUBLE $HRh(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_3$ IN SUPPORTED AQUEOUS-PHASE. IS IT REALLY AQUEOUS?

István T. HORVÁTH

Corporate Research Science Laboratories, Exxon Research and Engineering Company, Annandale, NJ 08801, U.S.A.

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The hydroformylation of olefins with the water soluble complex HRh(CO) $[P(m\text{-}C_6H_4SO_3Na)_3]_3$ ($\underline{1}$) is dependent on the solubility of the olefins in the aqueous phase. In contrast, when the aqueous solution of $\underline{1}$ is immobilized on a high surface area silica support the effects of the size of the olefins diminish. The immobilized catalyst $\underline{1}$ on silica shows significant water loss but not rhodium leaching. It is proposed that the hydrophilic support holds the water soluble phosphines by hydrogen bonding of the hydrated sodium-sulphonate groups to the surface.

The application of water soluble transition metal complexes for biphase catalytic reactions has attracted much attention [1]. The tris-(sodium m-sulfophenyl)-phosphine modified rhodium catalyst system has been used for the hydroformylation of propylene, and the major species present in the water phase is $HRh(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_3$ ($\underline{1}$) [2,3]. Unfortunately, the potential application of this system is limited by the solubility of the olefin in the water phase. The immobilization of an aqueous solution of $\underline{1}$ into a high surface area hydrophilic support by Arhancet, Davis, Merola and Hanson represents a major breakthrough, as the solubility of the olefin in the aqueous phase does not seem to be a limiting factor [4]. Octene-1, dicyclopentadiene, and even oleyl alcohol were easily hydroformylated. However, the selectivity toward linear nonanal in the hydroformylation of octene-1 with the supported aqueous-phase (SAP) catalyst was poorer than in the biphase systems. It has been suggested that during catalysis $\underline{1}$ remains dissolved in the aqueous phase and works at the aqueous-organic interphase [4]. Reported herein is the first comparative study of the biphase and SAP catalysts, which suggests that the water is an immobilization agent rather than a solvent in SAP.

Table 1
Hydroformylation of 1:1:1 mixture of hexene-1, octene-1, and decane-1 with water soluble $HRh(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_3$ (1)/$P(m\text{-}C_6H_4SO_3Na)_3$ in biphase and silica-supported aqueous phase, and with organic soluble $HRh(CO)(PPh_3)/PPh_3$

	$P(m\text{-}C_6H_4SO_3Na)_3$					PPh_3		
Rhodium [mmol]	0.75		0.1			0.1		
Phosphine [mmol]	13.5		0.7			0.7		
P/Rh	18		7			7		
H_2O [g]	34		1.0			–		
CPG-240 * [g]	–		6.0			–		
Olefins [mmol]	1100		51			51		
Hexane [g]	–		100			100		
Pressure [psi]	825		725			725		
Temperature [° C]	125		100			100		
Time [min]	1320	2680	5	15	65	1	3	10
Hexenes ** [%]	10.3	9.2	nd	nd	nd	1.3	1.2	0.9
Heptanals [%]	75.9	89.9	20.9	51.8	94.6	16.2	63.3	96.9
n/i	25.7	26.2	3.2	2.9	2.9	2.7	2.6	2.6
Octenes ** [%]	4.3	6.9	nd	nd	nd	0.9	0.9	0.5
Nonanals [%]	22.6	50.4	20.2	51.4	95.1	17.5	65.4	97.8
n/i	25.6	25.5	2.9	2.9	2.9	2.6	2.6	2.6
Decenes ** [%]	1.4	4.3	nd	nd	nd	0.7	0.5	0.5
Undecanals [%]	4.2	10.9	18.5	49.9	94.6	17.4	65.8	97.9
n/i	18.6	18.9	2.5	2.8	2.8	2.6	2.6	2.6

* Mean pore diameter 237 Å, pore distribution ±4.3%, pore volume 0.95 ml/g, surface area 77.5 m^2/g, particle size 120/200 MESH, product of CPG Inc, Fairfield, New Jersey, U.S.A.

** Internal-olefins.

$HRh(CO)[p(m\text{-}C_6H_4SO_3Na)_3]_3$ (1) was prepared by known methods [3,4]. The supported aqueous-phase (SAP) catalyst was prepared by the impregnation of an aqueous solution of 1 and free $P(m\text{-}C_6H_4SO_3Na)_3$ into CPG-240, a narrow pore size distribution silica (see footnote in table 1) [4]. The hydroformylation reactions were performed in a 300 mL stainless steel autoclave at constant pressure. During the use of the SAP catalyst a high pressure IR system and a membrane pump were connected to the autoclave through a dip-leg equipped with a 7μ filter. The reaction solution was continuously circulated from the reactor to the high pressure IR cell and back to the autoclave. The reactor was charged with the catalyst and the solvent under N_2 at 25 ° C, then heated to 100 ° C under 360 psi $H_2/CO(1:1)$. The olefins were charged at reaction pressure.

The hydroformylation of olefins with the biphase catalyst system was investigated to establish a basis for comparison. In order to monitor the role of the solubility of the olefins, a 1:1:1 mixture of hexene-1, octene-1 and decene-1 was used as the substrate. Since the catalytic activity of 1 is low at 100 ° C and 725 psi $H_2/CO(1:1)$ (the reported conditions for SAP [4]) further experiments were performed at 125 °C and 825 psi $H_2/CO(1:1)$ (table 1). As expected, the solubility of the olefins in the aqueous phase is an important factor in controlling the conversion to aldehydes and, to a lesser extent, to the *n/i* ratio. The high *n/i* ratio and the low reactivity suggest that the active species is $\{HRh(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_2\}$ containing two phosphines in trans position [3].

When the SAP catalyst (0.1 mmol $HRh(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_3$ (1a), 0.4 mmol $P(m\text{-}C_6H_4SO_3Na)_3$, 1.0 g H_2O, and 6.0 g CPG-240) and n-hexane (100 g) is charged with 360 psi of $CO/H_2(1:1)$ at 25 °C, the high pressure IR shows that some H_2O is already leached from the catalyst. During the heat up period to 100 °C, the amount of dissolved water in the solvent increases (fig. 1), as expected. Immediately after the addition of the olefin mixture at 725 psi $CO/H_2(1:1)$, the IR shows the presence of the olefins, an increased amount of CO, and a very small amount of aldehydes. The amount of aldehydes increases during the next 15 min while the olefin concentration decreases proportionally. The reaction is complete after 75 minutes. No spectroscopic evidence was found

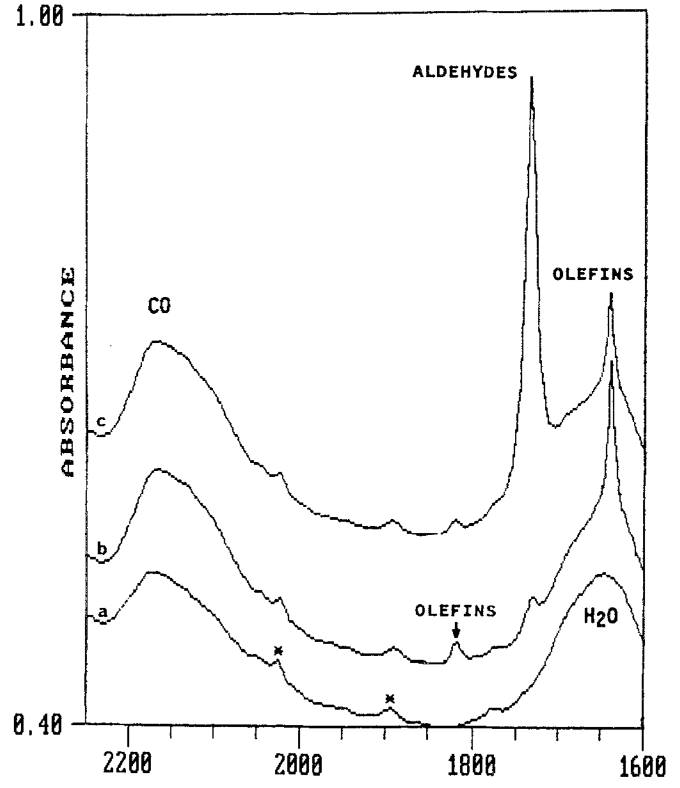

Fig. 1. High pressure FTIR spectra of the hexane solution (a) under 360 psi $H_2/CO(1:1)$ at 100 ° C (the small peaks marked with asterisks are due to n-hexane), (b) after the addition of the 1:1:1 mixture of hexene-1, octene-1, and decene-1 under 725 psi H_2/CO (1:1) at 100 ° C, and (c) after 15 min at 725 psi $H_2/CO(1:1)$ at 100 ° C.

for the presence of any rhodium-carbonyls in the solution prior to or during the reaction. Another leaching test was performed by using two autoclaves, both connected to the high pressure IR. In the first autoclave octene-1 was hydroformylated with the SAP catalyst up to 50% conversion. The solution was then pumped and filtered through the IR system at 725 psi $CO/H_2(1:1)$ and 100 °C into the second autoclave, leaving the SAP catalyst in the first one. The second autoclave also contained hexene-1. No further reaction was found for octene-1 and no reaction at all for hexene-1 in the next 24 hours. Thus it was unambiguously established that the SAP catalyst does not leach catalytically active rhodium species under hydroformylation conditions. The catalytic data for the hydroformylation of the olefin mixture with the SAP catalyst are reported in table 1. The remarkable similarities in conversions to aldehydes and the almost constant *n/i* ratio throughout the reaction clearly established that the solubility of the olefins in the water phase does not control the performance of the SAP catalyst. Interestingly, when the olefin mixture is hydroformylated with the organic soluble $HRh(CO)(PPh_3)_3/PPh_3$ system at the same conditions the results were very similar to those obtained with the SAP catalyst (table 1). Under milder conditions the only species present in the nonaqueous system is $HRh(CO)_2(PPh_3)_2$ [3, 5g], which could lead to either $\{HRh(CO)(PPh_3)_2\}$ ($\underline{A}$) or $(HRh(CO)_2(PPh_3))\}$ ($\underline{B}$), the two key intermediates in phosphine modified rhodium hydroformylation systems [5]. The *n/i* ratio of the aldehydes is largely controlled by the competitive reactions of the olefin with intermediates $\underline{A}$ and $\underline{B}$ resulting in high or low *n/i* ratio, respectively [5]. Therefore the observed low *n/i* ratio of the SAP system suggests that the active species may be the coordinatively unsaturated $\{HRh(CO)_2[P(m\text{-}C_6H_4SO_3Na)_3]\}$ [6].

The crucial test for the SAP catalyst was performed in a tubular trickle-bed reactor (ϕ 1/2″) at 100 °C and 725 psi $H_2/CO(1:1)$ using 3 g of SAP catalyst. The olefin mixture and the hexane solvent were not saturated with water. In the first 4 hours the catalytic data were very similar to those obtained in the batch reactor (50% conversion and 2.8 *n/i* ratio at 0.25 ml/min feed and 80 scc/min $H_2/CO(1:1)$ flow rate). However, in the next 10 hours the conversion increased to 100% and the *n/i* ratio decreased to 2.5. While the conversion remained the same for the next 24 hours, the *n/i* ratio decreased to 2.2. The reaction was stopped after 38 hours, while the catalyst was still active, for catalyst characteri-

Table 2
Water and elemental analysis of fresh and used SAP catalyst *

	H_2O [%]	Rh [%]	P [%]	S [%]
Fresh SAP	13.88	0.10	0.25	0.95
Used SAP	3.70	0.11	0.25	1.02
CPG-240	0.32			

* Performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, U.S.A.

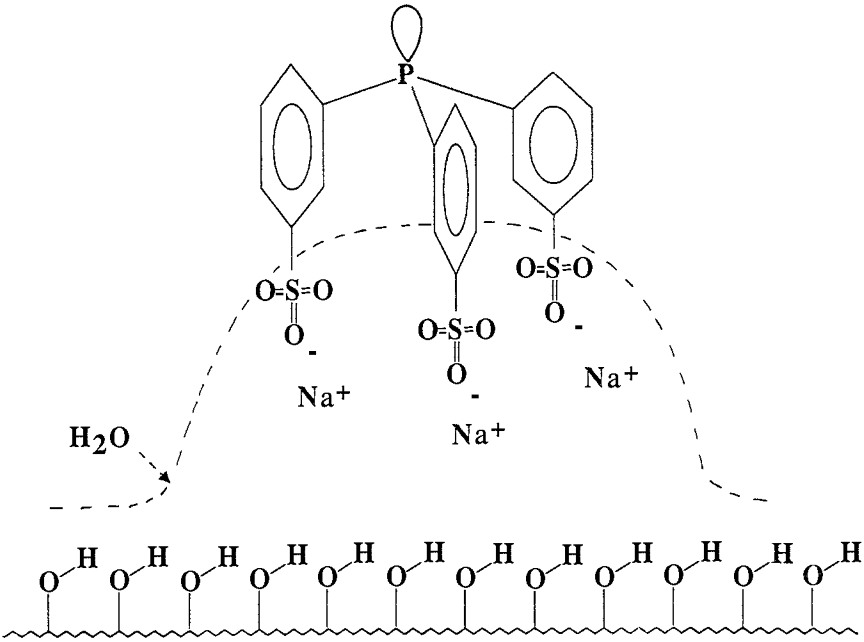

Fig. 2. Proposed immobilization of the water soluble $P(m\text{-}C_6H_4SO_3Na)_3$ on the hydrophilic support by hydrogen bonding of the hydrated sodium-sulphonate groups to the surface.

zation. Elemental and water analysis of the fresh and the used catalyst revealed that only water had leached from the catalyst (table 2). The amount of water remaining in the still active catalyst does not seem to be enough to provide a liquid aqueous phase thicker than two monolayers of H_2O on the SAP catalyst. Therefore, it is proposed that the hydrophilic support holds the water soluble phosphines by hydrogen bonding of the hydrated sodium-sulphonate groups to the surface (fig. 2).

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