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The effect of salt on selectivity in water soluble hydroformylation catalysts ☆

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Abstract

The hydroformylation of octene-1 under two-phase reaction conditions with rhodium catalysts derived from TPPTS (trisulfonated triphenylphosphine) or the new water soluble phosphines, $P[C_6H_4\text{-}p\text{-}(CH_2)_xC_6H_4\text{-}p\text{-}SO_3Na]_3$, $x=3$, 6, is salt concentration dependent. Both reaction rate and reaction selectivity are affected by the ionic strength of the aqueous reaction medium. Reaction selectivity increases with increased ionic strength while activity is dependent on whether the phosphine is capable of forming micelles. Reaction rate increases with increased ionic strength with the new surface active phosphines. The concentration of all components, free ligand, rhodium complex and salt affect the activation barrier to ligand exchange in $HRh(CO)(TPPTS)_3$ as determined by dynamic ^{31}P NMR spectroscopy. At low concentration with no added salt the barrier to exchange is estimated to be 22.4 kcal mol^{-1} whereas at high ligand and complex concentration the barrier is estimated to be 30.6 kcal mol^{-1}. It is proposed that high ionic strength stabilizes the complex, $HRh(CO)(TPPTS)_3$, in aqueous solution.

Keywords: Catalysis; Hydroformylation; Selectivity; Rhodium complexes

1. Introduction

Much has been written on aqueous phase catalysts derived from TPPTS [1–10]. An examination of the patent literature on hydroformylation catalysts derived from rhodium and TPPTS reveals that in nearly all reported patent examples an additional salt is added to the aqueous phase [7–10]. Typically these are either ionic surfactants or sodium phosphates, e.g. Na_2HPO_4; the role of the added ionic component is apparently to either improve mixing of the two phases, in the case of a surfactant, or to control the reaction pH. Included in the patents with specific examples are two substrates, propylene and hexene [7–10]. Both of these substrates yield a high proportion of linear aldehydes in the hydroformylation reaction. Separate high pressure NMR experiments and exchange reactions with free TPPTS have indicated a special stability for water soluble rhodium complexes of TPPTS [2]. Specifically it was shown that the dissociation of TPPTS from $HRh(CO)(TPPTS)_3$ has an activation barrier of 30.2 kcal mol^{-1}. For comparison previous NMR studies on the corresponding dissociation of PPh_3 from $HRh(CO)(PPh_3)_3$ estimated a 19 kcal mol^{-1} activation barrier for the exchange of the non-sulfonated phosphine [11]. The high barrier to ligand exchange in the TPPTS complexes was argued to be responsible for the high selectivity of these catalysts in the hydroformylation reaction. Specifically the reaction equilibria depicted in Scheme 1 lie in favor of $HRh(CO)(TPPTS)_3$ leading to catalysis via $HRh(CO)(TPPTS)_2$. This behavior was attributed to hydrogen bonding between sulfonate groups and water. Additionally under high CO pressure only $HRh(CO)(TPPTS)_3$ was observed by ^{31}P NMR spectroscopy [2].

$$HRh(CO)(TPPTS)_3 \underset{+TPPTS}{\overset{-TPPTS}{\rightleftharpoons}}$$

$$HRh(CO)(TPPTS)_2 \underset{-CO}{\overset{+CO}{\rightleftharpoons}} HRh(CO)_2(TPPTS)_2$$

Scheme 1.

Lower reaction selectivity has been observed for the water soluble catalysts under other reaction conditions. Notably, supported aqueous phase materials derived

☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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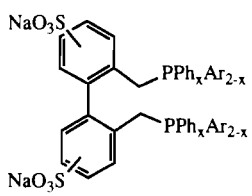
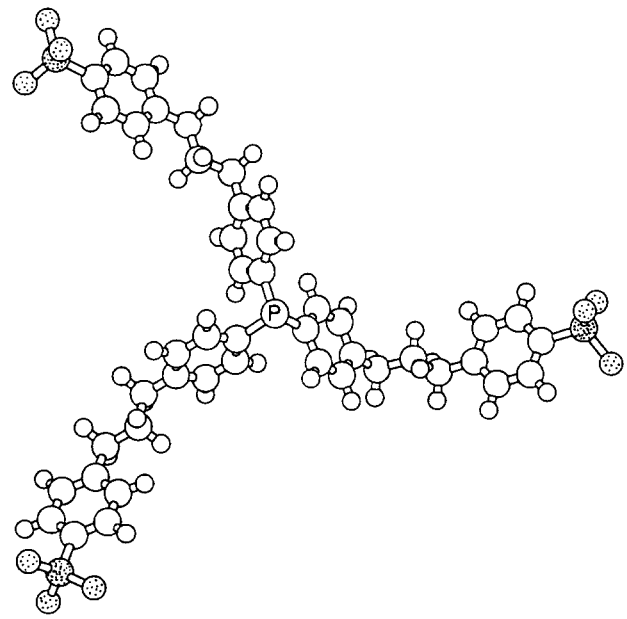
from $HRh(CO)(TPPTS)_3$ and TPPTS on controlled pore glass yield catalysts that give normal-to-branched (*n/b*) ratios most commonly in the range 2.5–5 for linear α olefins [12–15]. Similar selectivities are also observed when the rhodium catalyst is supported on ion exchange resins [16]. More recently in comparing the activity and selectivity of new surface active phosphines with TPPTS we find that our rhodium TPPTS catalysts give relatively poor selectivity (low *n/b* ratios) for the hydroformylation of octene-1 [17,18]. In surveying the results from our laboratory and in the literature we note that the catalysts that give poor reaction selectivity contain no added salt, buffer or surfactant. Exceptions to this are observed with phosphines other than TPPTS, for example, surface active sterically demanding phosphines can give relatively high *n/b* ratios without added salt [18]. Good selectivity is observed with the dinuclear rhodium complexes, $Rh_2(\mu\text{-}SR)_2(CO)_2(TPPTS)_2$ [3]. Also, sulfonated BISBI yields very selective water soluble hydroformylation catalysts [19]. Generally the aqueous solutions of the TPPTS catalysts that give poor selectivity have a relatively low ionic strength. Some of the catalytic solutions also contain methanol [17,18] which serves not only to improve mixing of the aqueous and non-aqueous phases but also to further lower the ionic strength of the aqueous phase.



sulfonated BISBI; Ar = m-$C_6H_4SO_3Na$

For the surface active phosphines, $P[C_6H_4\text{-}p\text{-}(CH_2)_xC_6H_4\text{-}p\text{-}SO_3Na]_3$, the degree of phosphine association in aqueous solution is dependent on salt concentration [18], while TPPTS in water shows no evidence for uniform aggregation with or without added salt. However, in the sense that $HRh(CO)(TPPTS)_3$ represents an aggregate of three TPPTS ligands it is likely that the ionic strength of solutions of $HRh(CO)(TPPTS)_3$ would influence its properties. Here we show that the ionic strength of aqueous solutions of $HRh(CO)(TPPTS)_3$ directly impacts reaction selectivity. Similar salt effects are observed with the surface active phosphines described above. Furthermore ionic strength affects the exchange of free and coordinated phosphine as determined by ^{31}P NMR spectroscopy. Dynamic light scattering however fails to detect $HRh(CO)(TPPTS)_3$ in aqueous solution.



surface active phosphine with $x=3$

2. Experimental

All catalytic reactions and sample manipulations were carried out using standard Schlenk techniques under an atmosphere of nitrogen or carbon monoxide. Solvents, including water, were distilled under nitrogen before use. Octene-1 and nonane (Aldrich) and $Rh(acac)(CO)_2$ (Strem) were used as received.

The high pressure hydroformylation reactions were done in 30 ml stainless steel reactors equipped with pressure gauges as previously described [17]. A Varian 3300 gas chromatograph equipped with an HP-1 column (25 m × 0.32 mm × 0.52 μm) and an FID detector were used for product analysis. The carrier gas was helium.

The catalytic reactions were done according to the following general procedure. Stock solutions of $Rh(acac)(CO)_2$ and the corresponding phosphine were prepared in water. In each case the concentration of Rh was 0.005 M and the phosphine concentration was varied to give the correct ligand to rhodium ratio. For each run 1.56 ml stock solution, 0.6 ml octene-1, and 0.34 ml nonane as an internal standard, were added to the reactor. For those reactions done in the presence of Na_2HPO_4, 0.209 g of the salt was added to the reactor. All transfers to the reactor were done under an atmosphere of CO. The vessel was then sealed and pressurized with CO/H_2, 1/1 to 14 atm. and immersed into a silicone oil bath preheated to 120 °C. All catalytic reactions reported in this paper were allowed to proceed for 24 h. At the end of the catalytic run the reactor was cooled to room temperature and analyzed by gas chromatography. For all the reactions reported the

overall conversion to aldehydes is low. Isomerization and hydrogenation side conversions are also low, less than 2% in each case.

Dynamic ^{31}P NMR spectroscopy was done at 161.903 MHz on a Varian RU 400 spectrometer. All spectra were recorded with high power proton decoupling. The number of scans varied from 32 to 128; more scans were required at high temperature to give satisfactory signal to noise ratios. The sample temperature was controlled and measured by a Varian temperature controller. The temperatures used in the analysis are those measured directly and are not corrected. At each temperature the sample was allowed to come to thermal equilibrium before data acquisition was initiated. This was judged to require 10 min after the temperature of the probe had stabilized. The natural linewidth of $HRh(CO(TPPTS)_3$ was estimated from the room temperature spectrum of the complex in the absence of added TPPTS.

3. Results and discussion

The hydroformylation of octene-1 with $HRh(CO)TPPTS_3$ under two-phase reaction conditions in the absence of methanol proceeds slowly. With methanol as a cosolvent octene-1 has improved solubility in the aqueous methanol phase and reaction rates are correspondingly better [18]. Reaction selectivity, as determined by the normal-to-branched ratio, however, does not exceed 4/1 even with a ten-fold excess of TPPTS. With water alone as the solvent the results are quite different. These are summarized in Table 1. Although conversions are lower than in the presence of methanol reaction, selectivity changes significantly; at a given TPPTS/Rh ratio selectivity is improved in water alone as the solvent compared to aqueous methanol.

High ionic strength is anticipated to decrease the already low solubility of octene-1 in water. For this reason alone rates are expected to be lower in catalysts that have high Na_2HPO_4 concentrations. This is indeed observed as seen from the data reported in Table 1. Unexpected, however, is the increase in reaction selectivity when the catalysis is done in the presence of high Na_2HPO_4 concentrations. At a TPPTS/Rh ratio of 10/1 the selectivity to linear aldehydes is >95% ($n/b = 24.1$) in the presence of Na_2HPO_4, compared to 92% linear ($n/b = 11.6$) in the absence of disodium phosphate. Since the conversion drops the difference in selectivity needs to be viewed with caution, however results obtained with the surface active phosphines (vide infra) suggest that the selectivity effect is real. At a TPPTS to Rh ratio of 3/1 a similar salt effect is observed (Table 1). Compared to the data with TPPTS in pure water the addition of the surfactant, SDS (sodium dodecylsulfate), increases the conversion but has little effect on selectivity. The presence of the surfactant gives the added complication of poor phase separation when the reaction is stopped. Also of interest is the increase in activity upon going from a TPPTS/Rh ratio of 3/1 to 10/1 without added salt. This must be somehow connected to the nature of the two-phase reaction conditions since in the unsulfonated catalyst system higher ligand to rhodium ratios decrease reaction rates.

As noted above the surface active phosphines, $P[C_6H_4\text{-}p\text{-}(CH_2)_xC_6H_4\text{-}p\text{-}SO_3Na]_3$, aggregate in aqueous salt solutions. The effect of salt on octene-1 hydroformylation with the phosphines, $x = 3$ and $x = 6$, was therefore studied. The results are summarized in Tables 2 and 3. At a L/Rh ratio of 3 reactivity increases slightly as the phosphine is made more surface active by the addition of methylene groups. There is little difference in reaction selectivity as the phosphine is changed. Reaction selectivity improves upon addition of Na_2HPO_4 to catalytic reactions of the surface active phosphines. Importantly the reaction rate, as indicated by conversion in a batch reaction, does not decrease rather it increases with the added salt. This is attributed to the fact that the surface active phosphines aggregate in aqueous salt media. As shown with TPPTS the addition of surfactants increases reaction rate by increasing the solubility of the substrate in the aqueous phase. Salt promotes the formation of micelles with the surface active phosphines and thus increases the reaction rate slightly. Since the conversion and selectivity both increase with these ligands this leads us to conclude that salt concentration has a real effect on reaction selectivity in water soluble hydroformylation catalysts.

Table 1
Hydroformylation of octene-1 with $TPPTS/Rh(acac)(CO)_2$ [a]

	TPPTS/Rh = 3		TPPTS/Rh = 10	
	Yield (%)	*n/b*	Yield (%)	*n/b*
TPPTS	10.4	4.0	19.3	11.6
TPPTS, 0.5 M Na_2HPO_4	3.7	8.4	7.7	24.1
TPPTS, 0.5 M SDS			43.0	9.4

[a] Reaction temperature, 120 °C. Pressure at 120 °C = 19.5 atm. Reaction time, 24 h. Octene-1/Rh = 500. [Rh] = 0.005 M.

Table 2
Hydroformylation of octene-1 with $P[C_6H_4\text{-}p\text{-}(CH_2)_3C_6H_4\text{-}p\text{-}SO_3Na]_3$/$Rh(acac)(CO)_2$ [a]

	L/Rh = 3	
	Yield (%)	*n/b*
$P[C_6H_4\text{-}p\text{-}(CH_2)_3H_4\text{-}p\text{-}SO_3Na]_3$	12.8	3.6
$P[C_6H_4\text{-}p\text{-}(CH_2)_3C_6H_4\text{-}p\text{-}SO_3Na]_3$, 0.5 M Na_2HPO_4	14.6	9.8

[a] Reaction temperature, 120 °C. Pressure at 120 °C = 19.5 atm. Reaction time, 24 h. Octene-1/Rh = 500. [Rh] = 0.005 M.

Table 3
Hydroformylation of octene-1 with $P[C_6H_4\text{-}p(CH_2)_6C_6H_4\text{-}p\text{-}SO_3Na]_3$/$Rh(acac)(CO)_2$ [a]

	L/Rh = 3	
	Yield (%)	*n/b*
$P[C_6H_4\text{-}p\text{-}(CH_2)_6C_6H_4\text{-}p\text{-}SO_3Na]_3$	19.1	3.4
$P[C_6H_4\text{-}p\text{-}(CH_2)_6C_6H_4\text{-}p\text{-}SO_3Na]_3$, 0.5 M Na_2HPO_4	24.2	8.6

[a] Reaction temperature, 120 °C. Pressure at 120 °C = 19.5 atm. Reaction time, 24 h. Octene-1/Rh = 500. [Rh] = 0.005 M.

Previously reported dynamic ^{31}P NMR data on the exchange of free and coordinated phosphine in the $HRh(CO)TPPTS_3$/TPPTS system do not indicate whether salt was added to the solutions nor are concentrations of reagents reported; the activation barrier for TPPTS was calculated from NMR data to be 30.2 kcal mol^{-1} [2]. In light of the catalytic results above we sought to investigate the effect of added salt on the activation energy for the dissociation of TPPTS from $HRh(CO)TPPTS_3$. The method follows that of Oswald and co-workers in their investigation of the dissociation of PPh_3 from $HRh(CO)(PPh_3)_3$; that is, the linewidth of the ^{31}P NMR signal of coordinated TPPTS in $HRh(CO)TPPTS_3$ in the presence of excess TPPTS was used to estimate the rate of exchange as a function of temperature [11]. Experiments were done under the following conditions: (i) 10 mM $HRh(CO)TPPTS_3$, and 60 mM TPPTS in D_2O; (ii) 10 mM $HRh(CO)TPPTS_3$, 60 mM TPPTS, and 100 mM Na_2SO_4 in D_2O; (iii) 100 mM $HRh(CO)TPPTS_3$, and 600 mM TPPTS in D_2O. For data in the temperature range 80–105 °C the calculated activation energies are 22.4, 25.8 and 30.6 kcal mol^{-1} for experiments (i), (ii) and (iii), respectively. The Arrhenius plots are shown in Fig. 1 for experiments (i) and (iii). Clearly the activation barrier for exchange is dependent on concentration of salt and total concentration of reagents. We propose that the critical parameter is the ionic strength of the solution since TPPTS, $HRh(CO)TPPTS_3$ and Na_2SO_4 are strong electrolytes. Thus the barrier to TPPTS dissociation increases with increasing ionic strength.

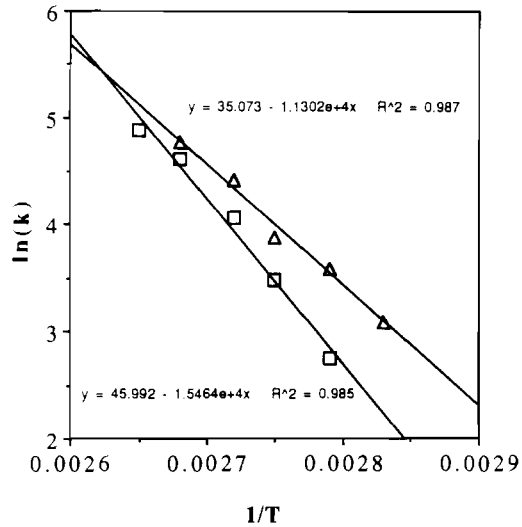


Fig. 1. Arrhenius plots for phosphine exchange in $HRh(CO)(TPPS)_3$ at 0.010 M Rh and 0.060 M TPPTS, triangles; 0.10 M Rh and 0.60 M TPPTS, squares.

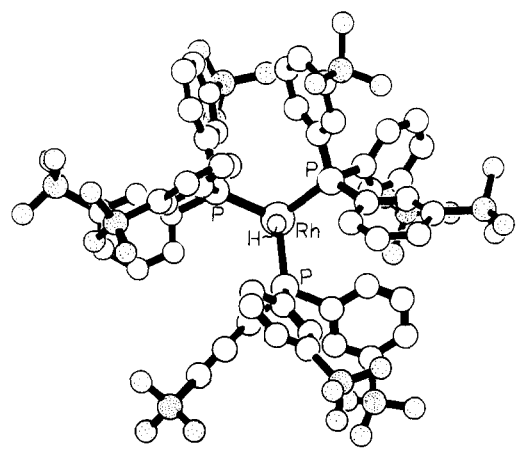


Fig. 2. Representation of $HRh(CO)(TPPTS)_3$ showing one possible arrangement of sulfonate groups in the TPPTS ligands. The sulfonate groups are shaded for clarity. The view is down the H–Rh bond.

We speculate that the data reported by Horvath et al. [2], which gave an activation barrier of 30.2 kcal mol^{-1}, were collected at relatively high ionic strength.

Micelles are stabilized in solutions of high ionic strength [20]. Although TPPTS has no tendency to aggregate in aqueous solution [18] the rhodium complex $HRh(CO)TPPTS_3$ approximates a molecular micelle. Dimensions for the TPPTS complex can be estimated from the crystal structure of the corresponding triphenylphosphine complex, $HRh(CO)(PPh_3)_3$ [21]. Using the atomic positions from this compound as a starting point one *meta* position on each of the nine phenyl groups was substituted by $[SO_3]^-$. Since there are two *meta* positions per phenyl ring and nine rings this leads to 2^9 possible conformations; shown in Fig. 2 is one conformation; it is derived from the orientation found in the solid state for $HRh(CO)(PPh_3)_3$ by substituting

at the *meta* position and requiring the sulfonate groups to be as far apart on average as possible. No attempt was made to minimize the structure for rotation about the P–C bonds and the structure is meant to give an estimate of the size of the molecule. The sulfonate groups can be considered to lie on the surface of a sphere of 8 Å in diameter. This is quite compact for a micelle with a net charge of −9. The close proximity of nine sulfonate groups in this compound should promote ligand dissociation to minimize electrostatic repulsions between sulfonate groups. We have shown that in the crystal structure of the sodium salt of $Co_2(CO)_6(TPPTS)_2$ sodium plays an important role in coordinating sulfonate groups in the solid state [22]. A complex network of hydrogen bonds and coordinated sodium cations is generated. Sodium and other ions are likely to play a similar role in solution. Thus we propose a refinement to the intramolecular hydrogen bonding model suggested by Horvath et al. [2]. Specifically we propose that the hydration sphere around $HRh(CO)TPPTS_3$ in aqueous solution is highly ordered and contains a high concentration of sodium cations to balance the charge on the rhodium TPPTS complex. High ionic strength stabilizes the hydration sphere by minimizing the electrostatic repulsions between sulfonate groups. Loss of a TPPTS ligand would require considerable reorganization of the solvation sphere and is thus unfavorable and is expected to become even more unfavorable as the ionic strength of the solution increases. This mechanism implies that reaction activity and selectivity may be dependent on the nature of the cation. Experiments are in progress with lithium and potassium salts of TPPTS.

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