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Anion effects in the formation of the active catalyst in the Ruhrchemie – Rhône-Poulenc aqueous biphasic hydroformylation process. Are there any?[1]

József Kovács, Ferenc Joó, and Carl D. Frohning

Abstract: The water soluble [Rh(OAc)(CO)(*m*tppms)$_2$] containing monosulfonated triphenylphosphine ligands was prepared for the first time and its hydrogenation was studied in aqueous solutions. In the presence of additional *m*tppms, the reaction yielded [RhH(CO)(*m*tppms)$_3$], a close analogue of [RhH(CO)(*m*tppts)$_3$], the immediate catalyst precursor in the Ruhrchemie – Rhône-Poulenc aqueous biphasic hydroformylation process. The extent of the [Rh(OAc)(CO)(*m*tppms)$_2$] → [RhH(CO)(*m*tppms)$_3$] transformation strongly depended on the solution pH, similar to the case of the hydrogenation of [RhCl(CO)(*m*tppms)$_2$] studied earlier. In this respect, $RhCl_3$·aq and $Rh(OAc)_3$·aq can be used equally well for the in situ preformation of [RhH(CO)(*m*tppts)$_3$], although the latter is the preferred choice in the industrial process.

Key words: rhodium, water-soluble, hydrides, sulfonated phosphines, biphasic.

Résumé : On a préparé pour la première fois les complexes [Rh(OAc)(CO)(*m*tppms)$_2$] qui sont solubles dans l'eau et qui contiennent des ligands triphénylphosphines monosulfonées et on a étudié leur hydrogénation dans des conditions aqueuses. En présence de *m*tppms additionnel, la réaction a conduit à la formation du [RhH(CO)(*m*tppms)$_3$], un analogue apparenté au [RhH(CO)(*m*tppts)$_3$], le précurseur immédiat du catalyseur utilisé dans le procédé d'hydroformylation biphasique aqueuse de la société Ruhrchemie – Rhône-Poulenc. Le degré de transformation de [Rh(OAc)(CO(*m*tppms)$_2$] → [RhH(CO)(*m*tppms)$_3$] dépend fortement du pH de la solution, ce qui est semblable à ce qui a été observé antérieurement dans le cas de l'hydrogénation du [RhCl(CO)(*m*tppms)$_2$]. À cet effet, le $RhCl_3$·aq et le $Rh(OAc)_3$·aq peuvent être utilisés aussi bien l'un que l'autre pour la préformation in situ du [RhH(CO)(*m*tppts)$_3$], même si le dernier est préféré dans le procédé industriel.

Mots clés : rhodium, soluble dans l'eau, hydrures, phosphines sulfonées, biphasique.

[Traduit par la Rédaction]

Introduction

The Ruhrchemie – Rhône-Poulenc process for the aqueous/organic biphasic hydroformylation of propene (1–3) was introduced into the industrial scene more than two decades ago. The key to the success of this process was the invention of an utterly hydrophilic, active, and stable catalyst [RhH(CO)(*m*tppts)$_3$] (*m*tppts = 3,3′,3″-phosphinetriylbenzenesulfonic acid, *meta*-trisulfonated triphenylphosphine) (4). In practice, the catalyst is *preformed* from suitable precursors, most commonly from hydrated rhodium(III) acetate and *m*tppts under synthesis gas pressure, and used without isolation (5). Under actual hydroformylation conditions, [RhH(CO)(*m*tppts)$_3$] is involved in various chemical equilib-

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ria, leading to the formation of $[RhH(CO)_2(mtppts)_2]$, $[RhH(CO)_2(mtppts)]$, and $[RhH(CO)(mtppts)_2]$ (2–5). Of these compounds, $[RhH(CO)(mtppts)_2]$ is the active catalyst for the formation of linear products, and these equilibria have been studied in detail (6) to obtain optimum rate and selectivity performance of the in situ formed catalyst.

Despite the continuous research and development, a few questions with regard to the reaction mechanism still deserve scrutiny. One of these is the effect of pH on the rate of hydroformylation. It is known that an increase in pH from 5.5 to 7.5 brings about a 35% increase in the reaction rate of the hydroformylation of propene (1). A similar rate increase was observed in the reaction of octene-1 (7). Since the chemical reaction does not involve H^+ or OH^-, the answer may involve the pH-sensitivity of the formation and further equilibria of the catalytically active rhodium complexes.

Some time ago, it was shown that the hydrogenation of the related, water-soluble $[RhCl(CO)(mtppms)_2]$ complex (*m*tppms = (3-diphenylphosphino)benzenesulfonic acid, *meta*-monosulfonated triphenylphosphine) in aqueous solution was, indeed, governed by the pH (8). In the presence of excess *m*tppms and chloride, the hydrogenation of $[RhCl(CO)(mtppms)_2]$ to yield $[RhH(CO)(mtppms)_3]$ did not take place below pH 4.5 but reached 100% conversion at pH 10. Importantly, at basicities between pH 5 and 8, the conversion increased gradually with the gradual increase of pH, and that referred to a pH-dependent mobile equilibrium (eq. [1]).

$$[1] \quad [RhCl(CO)(mtppms)_2] + mtppms + H_2 = [RhH(CO)(mtppms)_3] + H^+ + Cl^-$$

Although the conditions of this model study and those of the industrial hydroformylation strongly differ, one may expect similar equilibria be involved in the pH dependence of the hydroformylation reaction. However, albeit hydrated $RhCl_3$ is a suitable starting material for the synthesis of $[RhH(CO)(mtppts)_3]$, industry prefers $Rh(OAc)_3$·aq ($OAc^- = CH_3COO^-$) for the preformation of the catalyst to avoid the presence of the strongly nucleophilic chloride (4, 5). On the contrary, the pH-static hydrogenations [8] were performed at constant ionic strength maintained by KCl. The question arose, therefore, whether it is justified to draw conclusions regarding the pH effects on the formation of $[RhH(CO)(mtppts)_3]$ based on studies of chloride-containing systems, or to put it another way, whether there is an effect of the anion of the precursor on the formation of this hydroformylation catalyst. In the following, we report the results of a pH-static hydrogenation study of $[Rh(OAc)(CO)(mtppms)_2]$ under chloride-free conditions.

Experimental

All manipulations were done under an argon or nitrogen atmosphere. All solvents were purified by distillation and carefully deaerated before use.

IR spectra were recorded on a PerkinElmer Paragon 1000 PC FT-IR spectrometer in KBr discs. ^1H and ^{31}P NMR spectra were recorded on Bruker AV 360 equipment in D_2O or $(CD_3)_2SO$ (DMSO-d_6). Chemical shifts are referenced to residual solvent peaks further referenced to external 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) sodium salt (^1H) and 85% H_3PO_4 (^{31}P), respectively. Conditions of the pH-potentiometric measurements are described in detail in refs. 9 and 10.

$RhCl_3$·aq was purchased from the Pressure Chemical Co. (Pittsburgh, Pennsylvania), D_2O and DMSO-d_6 from Cambridge Isotope Laboratories, and H_2, N_2, Ar, and CO from Linde (Hungary). Other reagents were obtained from Aldrich and used without further purification. *m*tppms (Na^+-salt) (11) and $[Rh(OAc)_2]_2$·2MeOH (12) were prepared as described in the literature.

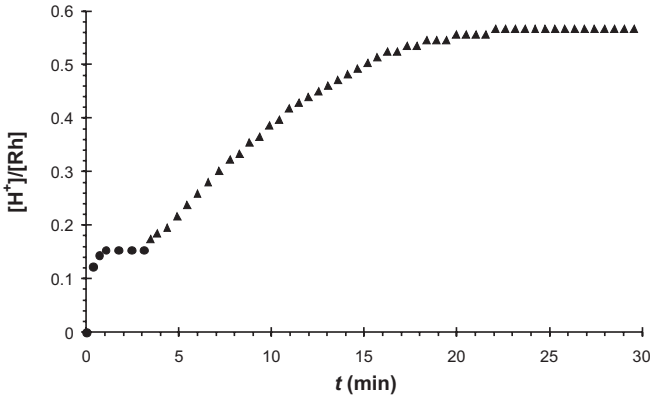
$[Rh(OAc)(CO)(mtppms)_2]$ was prepared by a modification of the literature method (13) for the synthesis of $[Rh(OAc)(CO)(PPh_3)_2]$. To a suspension of 0.1 g (0.4 mmol Rh) $[Rh(OAc)_2]_2$·2MeOH in 10 mL ethanol was added 0.25 mL of 50% HBF_4 and the solution was stirred at 60 °C for 20 h. To the resulting green solution, a solution of 640 mg (1.6 mmol) *m*tppms and 545 mg (4 mmol) $NaOAc·3H_2O$ in 10 mL ethanol was added at room temperature and the mixture was refluxed for 3 h. An orange solid separated that was filtered and washed with ethanol. This raw product ($[Rh(OAc)(mtppms)_3]$ together with inorganic impurities, NaOAc, $NaBF_4$) can be directly used for further synthesis. It was suspended in 5 mL of fresh ethanol, and bubbled with CO at room temperature, upon which the color changed gradually to orange then to yellow with dissolution of the solid. The reaction with CO overnight gave a cream-coloured precipitate. The *complex* was filtered, washed with ethanol, and dried. Weight: 300 mg (67% overall yield). IR (cm^{-1}): 1978 ν(CO), 1399 ν_s(COO), 1579 ν_{as}(COO), 1038, 1195 ν(SO_3). ^1H NMR (360 MHz, DMSO-d_6, r.t., ppm) δ: 0.67 (s, CH_3COO), 6 to 7 (m, aromatic protons). ^{31}P NMR (360 MHz, DMSO-d_6, r.t., ppm) δ: 35.3 (d, ^1J(Rh-P) = 138 Hz). Anal. calcd. (%): C 47.28, H 3.97, S 6.47; found: C 46.30, H 4.07, S 6.49.

Results and discussion

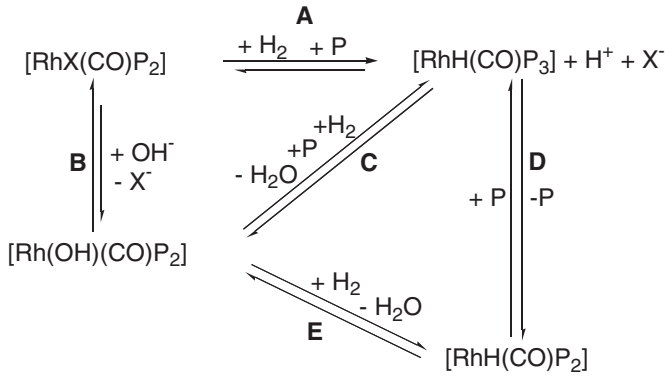
$[Rh(OAc)(CO)(mtppms)_2]$ was synthesized for the first time by a modified procedure of Mitchell et al. (13) for the synthesis of $[Rh(OAc)(CO)(PPh_3)_2]$, based on the reaction of the green dirhodium(II) cation (Rh_2^{4+}) with *m*tppms) followed by carbonylation with CO. Replacement of PPh_3 with *m*tppms in the procedure described by Spencer (14) for the preparation of $[Rh(OAc)(PPh_3)_3]$ from $RhCl_3$·aq did not yield the expected acetatorhodium(I) complex, but afforded $[RhCl(mtppms)_3]$. The cream-coloured $[Rh(OAc)(CO)(mtppms)_2]$ dissolves well in water and in DMSO, but is only slightly soluble in ethanol and insoluble in apolar organic solvents. According to the IR and NMR spectra, it has a square-planar geometry with a monodentate acetato ligand (ν_{as}(COO) – ν_s(COO) = 180 cm^{-1}) (15) and with the phosphine ligands in the trans position.

Aqueous solutions of $[Rh(OAc)(CO)(mtppms)_2]$ react with H_2 and in the presence of excess *m*tppms yield the known $[RhH(CO)(mtppms)_3]$ (8, 16). This reaction was studied in a pH-static hydrogenation apparatus as described in detail for $[RhH(CO)(mtppms)_3]$ (8). Briefly, the pH of the deoxygenated solvent (0.1 mol/L $NaClO_4$ to maintain constant ionic strength) was set to a given value in the range $4 < pH < 10$ using $HClO_4$ or KOH, and a known amount of the complex was dissolved in it under an argon atmosphere. De-

Fig. 1. Proton production upon dissolution (●) and subsequent hydrogenation (▲) of [Rh(OAc)(CO)(*m*tppms)$_2$]. [Rh] = 1.8 mmol/L, [*m*tppms] = 5.4 mmol/L, [$NaClO_4$] = 0.1 mol/L, pH = 7.0, $p(H_2)$ = 1 bar (1 bar = 100 kPa), T = room temperature.



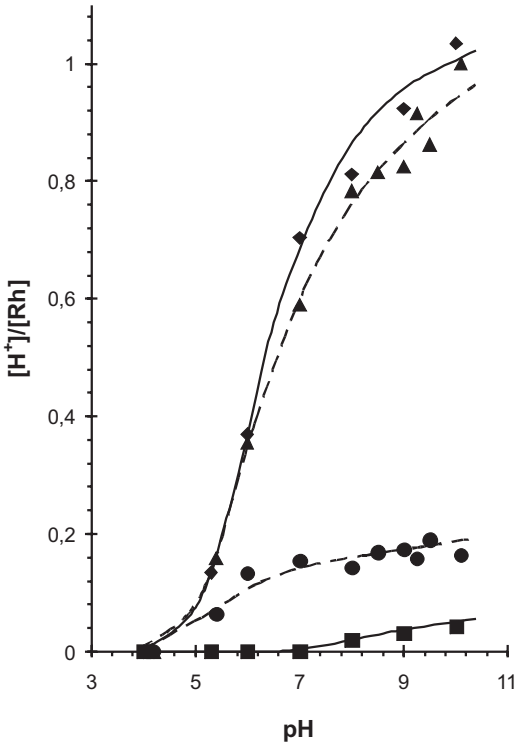
Scheme 1. Equilibria in solutions of [RhX(CO)P$_2$] (X = OAc$^-$ or Cl$^-$, P = *m*tppms) under H_2 in the presence of excess *m*tppms.



pending on the actual pH, hydrolysis of the complex to [Rh(OH)(CO)(*m*tppms)$_2$], the *m*tppts analog of which is described in ref. 17, occurred to a certain extent, resulting in proton release to the solution. However, the acid formed in this reaction was neutralized by KOH supplied by the autoburette and the pH remained constant; furthermore, the extent of hydrolysis could be calculated from the volume (amount) of KOH consumed. Figure 1 shows such a "titration curve" and the first "step" on the graph refers to the hydrolysis of the complex under an inert atmosphere (at the particular pH, i.e., 7.0 used in the experiment). Bubbling H_2 through the equilibrated solution resulted in further KOH consumption, indicating a heterolytic split of H_2 in its reaction with [Rh(OAc)(CO)(*m*tppms)$_2$] (and with [Rh(OH)(CO)(*m*tppms)$_2$] produced by the partial hydrolysis). This is the second step on Fig. 1. The reactions involved are shown on Scheme 1. Of particular interest is the fact that at this pH, the [H$^+$]/[Rh] ratio levels off at about 0.55 showing that only 55% (i.e., by far less than 100%) of all Rh reacted to yield [RhH(CO)(*m*tppms)$_3$].

Similar measurements were made at several pH values and the results are shown on Fig. 2. It is seen that [Rh(OAc)(CO)(*m*tppms)$_2$] does not react with H_2 below pH 4. However, the [H$^+$]/[Rh] ratio increases steadily with

Fig. 2. Proton production upon dissolution (●, ■) and subsequent hydrogenation (▲, ◆) of [Rh(OAc)(CO)(*m*tppms)$_2$] (●, ▲) and [RhCl(CO)(*m*tppms)$_2$] (■, ◆) at various pH. Conditions (●, ▲): [Rh] = 1.8 mmol/L, [*m*tppms] = 5.4 mmol/L, [$NaClO_4$] = 0.1 mol/L, $p(H_2)$ = 1 bar (1 bar = 100 kPa), T = room temperature; (■, ◆): [Rh] = 2.4 mmol/L, [*m*tppms] = 7.2 mmol/L, [$NaClO_4$] = 0.1 mol/L, $p(H_2)$ = 1 bar (1 bar = 100 kPa), T = 35 °C.



increasing pH showing that the reaction goes more and more extensively towards the formation of [RhH(CO)(*m*tppms)$_3$], reaching a practically complete conversion at pH 10. It is important to note that all reactions in Scheme 1 are reversible, and the pH-static hydrogenations reveal the extent to which [Rh(OAc)(CO)(*m*tppms)$_2$] (together with [Rh(OH)(CO)(*m*tppms)$_2$]) are converted to [RhH(CO)(*m*tppms)$_3$]. This extent is strongly pH dependent. Taking the closely similar chemical properties of *m*tppms and *m*tppts, we may assume that during the preformation of the catalyst in the Ruhrchemie – Rhône-Poulenc process [RhH(CO)(*m*tppts)$_3$] takes part in similar equilibria. Since [RhH(CO)(*m*tppts)$_3$] is the immediate precursor of the true hydroformylation catalysts (under syngas [RhH(CO)$_2$(*m*tppts)] and [RhH(CO)(*m*tppts)$_2$]), the actual proportion of rhodium that may enter the catalytic cycle(s) is strongly influenced by the pH, and this explains (at least in part) the higher catalytic activities observed at pH 7.5 vs. 5.5.

Data of the pH-static hydrogenation of [RhCl(CO)(*m*tppms)$_2$] are also shown in Fig. 2 for comparison. It can be concluded that there is no substantial effect of the anionic ligand (Cl$^-$ or OAc$^-$) on the pH dependence of the formation of [RhH(CO)(*m*tppms)$_3$]. In aqueous solutions, the heterolytic split of H_2 by transition metal complexes (such as shown by rxn. [1] and Scheme 1) is largely facilitated (18, 19) by the strong

hydration of the resulting H^+, $\Delta H^\circ_{hyd} = -1091$ kJ mol^{-1} (20), and the particular anion. It seems that the relatively small difference in the hydration ethalpies of Cl^- and OAc^-, –381 kJ mol^{-1} (20) and –334 kJ mol^{-1} (21), respectively, does not modify substantially the overall energy balance. The hydration enthalpy of OH^-, $\Delta H^\circ_{hyd} = -460$ kJ mol^{-1} (20), is higher than that of Cl^- and OAc^-; furthermore, formation of H_2O adds an additional driving force to reaction **E** (Scheme 1), so [Rh(OH)(CO)(*m*tppms)$_2$] is expected to react preferentially over [Rh(OAc)(CO)(*m*tppms)$_2$] and [RhCl(CO)(*m*tppms)$_2$]. Whether [RhH(CO)(*m*tppms)$_3$] (the resting state of the catalyst at high phosphine concentrations) is formed on path **A**, on path (**B** + **C**), or on path (**A** + **E** + **D**) is not known from these investigations, but its equilibrium concentration is pH-governed, independent of the way of formation. [Rh(CO)(OAc)(*m*tppms)$_2$] shows a somewhat higher tendency towards hydrolysis than [RhCl(CO)(*m*tppms)$_2$], although at room temperature, the extent of this hydrolysis does not exceed 20%.

Based on the above findings, it can be concluded that the pH of the aqueous phase has the same effect on the catalytic activity of Rh(I)-carbonyl-hydrides independent of the anion of the precursor being chloride or acetate. Nevertheless, the industrial preference for Rh(III)-acetate may be justified on other grounds, e.g., less corrosion or more favourable kinetics of the preformation of the catalyst. It is understood that the chemistry going on in the industrial hydroformylation reactor is far more complex than that described in this communication, and that the operational conditions of the Ruhrchemie – Rhône-Poulenc process for the aqueous/organic biphasic hydroformylation of propene (120 °C, 50 bar syngas (1 bar = 100 kPa)) are far from those of our measurements. This may influence the *positions* of the equilibria on Scheme 1, however, no other species were detected under pressure in case of the related *m*tppts complexes (6). Therefore, we think that the pH effects observed under more realistic hydroformylation conditions (1, 7) can also be related to the base-promoted formation of the actual hydroformylation catalysts, [RhH(CO)$_2$(*m*tppts)] and [RhH(CO)(*m*tppts)$_2$], as described previously.

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