

Redox chemistry of Pd^{2+} , Pt^{2+} , Rh^{3+} –TPPTS systems in water: pH influence on the preparation of low valent TPPTS complexes

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Abstract

The redox process of the water-soluble systems: TPPTS– $\text{Pd}(\text{OAc})_2$, PdSO_4 , PtCl_2 , $\text{Rh}_2(\text{SO}_4)_3$, and RhCl_3 , have been investigated at room temperature by ^{31}P -NMR spectroscopy, polarography and pH measurement. (TPPTS: 3,3',3''-phosphinidynetris(benzenesulfonic acid) trisodium salt, or the usual name: tris(*m*-sulfophenyl)phosphine trisodium salt). For a particular given value of pH, controlled by NaOH addition, except for $\text{Rh}_2(\text{SO}_4)_3$ which leads to a $\text{Rh}(\text{OH})_3$ precipitate, every system evolved very quickly, producing quantitatively OTPPTS (TPPTS oxide) and the metallic complexes with TPPTS in a reduced state: $\text{Pd}(\text{TPPTS})_n$ at $\text{pH} > 5$; $\text{Pt}(\text{TPPTS})_{n+1}$ at $\text{pH} > 7$; $[\text{Rh}(\text{TPPTS})_n]^+$ at $7 < \text{pH} < 13$, n ranging between 2 and 3. With Pd(II) and Pt(II) which are complexed in the oxidized state, the hydroxide ion intervenes probably to accelerate the disproportionation of an hydroxo species such as $\text{MOH}(\text{TPPTS})_n^+$ into OTPPTS and a low valence state metal complex: $\text{OH}^- + \text{HOM}(\text{TPPTS})_n^+ \rightarrow \text{M}(\text{TPPTS})_{n-1} + \text{OTPPTS} + \text{H}_2\text{O}$. The fact that TPPTS complexation by Rh(III) is not observed, implies that the different hydroxochloro Rh(III) species react directly with TPPTS to produce OTPPTS and Rh(I) which is subsequently complexed by TPPTS. © 1998 Elsevier Science B.V.

Keywords: TPPTS; Water-soluble catalysts; Oxidoreduction; Pd; Pt; Rh

1. Introduction

The use of water-soluble transition metal complexes with, e.g., TPPMS-(*m*-sulfophenyl) diphenylphosphine sodium salt [1] and TPPTS [2] ligands in water and in two phase systems has been gaining in importance since the first publications in 1975.

The scientific and industrial interest since then has led to the writing of more than 200 publications from numerous countries [3–5].

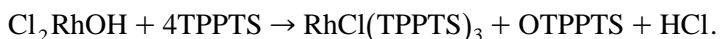
The development of industrial processes has been accompanied by a lot of scientific research, notably the synthesis of metallic complexes containing the TPPTS ligand. We can mention, chronologically, the different studies on the complexes of ruthenium, osmium and iridium [6,7], rhodium [8–12], molybdenum [10], palladium [10] and platinum [9].

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A lot of work has been done on the purification of TPPTS and its metallic complexes (e.g., Mn, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Ag, Au). Gel permeation chromatography has permitted the preparation of both analytically pure TPPTS and 40 associated metallic complexes [13–16]. The $\text{Pd}(\text{TPPTS})_3$, $\text{Pt}(\text{TPPTS})_4$ and $\text{XRh}(\text{TPPTS})_3$ [$\text{X} = \text{OH}, \text{Cl}$] complexes were characterized in particular by ^{31}P -NMR spectroscopy.

The syntheses of low valent complexes are often carried out by replacing other ligands such as CO, THF or TPP by TPPTS molecules. TPPTS also has the particularity of reducing the oxidized state of certain noble metal salts and at the same time of complexing with the reduced state.

The reduction of RhCl_3 by TPPTS has been studied in acidic medium [8,11]:



The reduction is slow: 70% conversion after 2.5 h reaction time at room temperature.

The reactivity of the RuCl_3 -TPPTS system in water solution is also low [17].

However, the synthesis of some oxidized complexes has also been carried out. $\text{PtCl}_2(\text{TPPTS})_2$ has been prepared by directly mixing K_2PtCl_4 and TPPTS in an aqueous solution [10,14–16]. The yield of this reaction is excellent: 96% without oxidation of TPPTS [14–16]. The homologue $\text{PdCl}_2(\text{TPPTS})_2$ has also been prepared from $\text{PdCl}_2(\text{PhCN})_2$ under the same conditions [18].

The formation of the $\text{Pd}(\text{OAc})_2(\text{TPPTS})_2$ complex has also been observed in the acetonitrile–water system (volume ratio of 11:1) [19], in the presence of tetrabutylammonium tetrafluoroborate, palladium acetate is reduced to $\text{Pd}(\text{TPPTS})_3$ in 0.5 h at room temperature [19]. More recently, $\text{Pd}(\text{TPPTS})_3$ has been prepared from PdCl_2 and TPPTS in 8 days at 25°C. An intermediate cationic complex $^+\text{PdCl}(\text{TPPTS})_3$ has been characterized [20].

In non-aqueous systems, the influence of the addition of alkali has been clearly observed in the reduction of Pd(II) to Pd(0) in the presence of arylphosphine [21].

As already mentioned, the conditions governing the oxido-reduction of these systems in water are not well defined. Under certain particular conditions no reaction occurs. In acidic media an overproduction of OTPPTS occurs during the reduction of Rh(III) [8]. This present work describes the detailed conditions which allow a rapid and selective reduction of rhodium, palladium and platinum salts by TPPTS. Thus well defined, low valent TPPTS complexes can subsequently be used as catalysts.

2. Results and discussion

We have essentially studied these systems using ^{31}P -NMR spectroscopy, potentiometry and polarography. The metallic salt concentrations used were around $1\text{--}6 \times 10^{-2}$ mol/l for potentiometry and NMR spectroscopy and $3\text{--}4 \times 10^{-4}$ mol/l for polarography. The initial molar ratio of TPPTS to the metal salt was between 2 and 7. An excess of TPPTS causes a dynamic equilibrium between free TPPTS and complexes, as shown by NMR spectroscopy.

In the case of oxidation of TPPTS, there is automatically an increase of the acidity. The measurement of pH along the whole experiment, allows the evaluation of the stability of the different systems:



The $\text{Pd}(\text{OAc})_2$ -TPPTS system has an initial pH = 6 but it is subject to a slow change down to pH = 4 after several hours.

Table 1
TPPTS–metallic salt solution properties

Salts	Initial pH ^a	pH evolution	Complexation of oxidised state ^c
Pd(OAc) ₂	6–7	↘ to 4	yes
PdSO ₄	2	↘ below 2	yes
PtCl ₂ + KCl	6–7 ^b	stable	yes
PtCl ₂	3–4 ^b	stable	yes
Rh ₂ (SO ₄) ₃	2	stable	no
RhCl ₃	2	↘ below 2	no

^aIn a Schlenk tube under argon equipped with a pH electrode, metallic salt is added to a 0.1 M TPPTS water solution (TPPTS/salt = 4:1).

^bPtCl₂ solubilized at 60°C.

^c³¹P-NMR and polarographic studies.

The pH of RhCl₃–TPPTS and PdSO₄–TPPTS systems is immediately acid (pH = 2 to 2.5) and changes continuously over time, becoming more acidic (around pH = 1.3 to 2).

After total dissolution, the pH of the PtCl₂–TPPTS system is stable (Table 1). After total mixing of TPPTS solution and a Rh₂(SO₄)₃ acidic solution the pH is near 2–2.5 but does not change.

2.1. PtCl₂–KCl–TPPTS and PtCl₂–TPPTS

PtCl₂ slowly dissolves at 60°C in a water solution of TPPTS and KCl (PtCl₂ = 3.75 × 10⁻² M; TPPTS/KCl/PtCl₂ = 4:10:1). After dissolving and cooling at room temperature the pH is 6.63. NMR analysis shows the presence of the complex PtCl₂(TPPTS)₂ previously described [3,10,4,5]. Another non-identified complex also appears δ = +24.37. OTPPTS is not produced during the dissolution.

Without KCl the results are similar (PtCl₂ = 5 × 10⁻² M; TPPTS/PtCl₂ = 4.26; solution S). After dissolving at 60°C and cooling at room temperature the pH is 3.5. The NMR spectrum is similar to the preceding one with PtCl₂(TPPTS)₂ and the peaks due to the non-identified complex. The zerovalent platinum complex Pt(TPPTS)₃ does not appear and a very small oxidation to OTPPTS is noticed (2%). The electrochemical study of the solution S was carried out in 0.1 M NaNO₃. The platinum salt concentration was 4 × 10⁻⁴ M. The pH was found stable before the NaOH addition (pH = 4.9).

Using differential pulse polarography (DPP) the TPPTS/PtCl₂ system exhibited a peak at -0.7 V/SCE, the shape of which indicating clearly that probably two species were present as previously observed by NMR spectroscopy before any addition of NaOH. Addition of NaOH modified this peak, since it decreased and appeared to be unique through loss of the first one (Fig. 1). This addition of NaOH corresponds quantitatively to half the initial amount of Pt. A further addition of NaOH

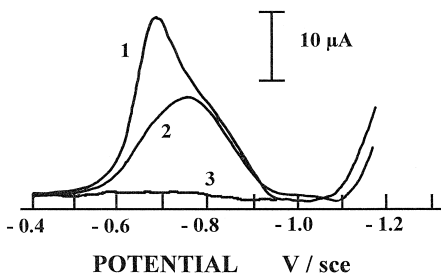


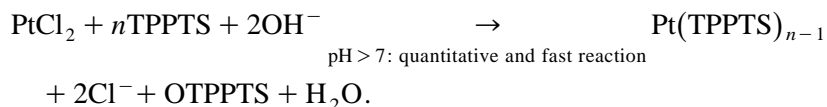
Fig. 1. DPP curves for PtCl₂–TPPTS system. (1) [PtCl₂] = 3.96 × 10⁻⁴ M and [TPPTS] = 1.69 × 10⁻³ M. (2) After NaOH addition: [NaOH]/[PtCl₂] = 1. (3) After NaOH addition: [NaOH]/[PtCl₂] = 2.

completely eliminated the peak. From these observations one may conclude that two platinum complexes were present at the beginning and that they were progressively destroyed as the pH increased.

Adding 0.4 M NaOH to the solution S, the pH rises to 10. After 3 min the pH falls back to 7.4. This procedure can be repeated several times ($\text{NaOH}/\text{PtCl}_2 = 2$).

The production of the platinum zero complex and OTPPTS is quantitative. The NMR analysis is in accordance with Refs. [14–16].

In conclusion, the system PtCl_2 –TPPTS which is very stable at slightly acid pH, is very reactive in a slightly alkaline medium. The platinum zero TPPTS complex is produced in quantitative yield as follows:



2.2. $\text{Pd}(\text{OAc})_2$ –TPPTS and PdSO_4 –TPPTS

At room temperature the pH of this system is recorded ($\text{Pd}(\text{OAc})_2 = 4.4 \times 10^{-2} \text{ M}$ –TPPTS/Pd = 3.87) (Fig. 2). The initial pH 6.25 drops to 4.67 during the first 5 min then varies slowly to 4.03 after 3 h.

The NMR spectrum of this aqueous solution exhibited 8 signals without the characteristic signal of the palladium zero complex. There is an exchange between TPPTS and the different species. The OTPPTS concentration slowly increases with time.

Indeed, the NMR spectrum of this system in an ethanol–water mixture (50–50) at -25°C shows the presence of the palladium zero complex: $\text{Pd}(\text{TPPTS})_3$ $\delta = +23.99$, TPPTS $\delta = -5.74$, OTPPTS $\delta = +31.18$ and 3 signals due to palladium species $\delta = +25.83$, $\delta = +28.60$, $\delta = +35.18$.

Then, 3 h after the beginning of the reaction, 0.4 M NaOH is added over a short period of time ($\text{NaOH}/\text{Pd} = 2$). The pH stabilized at 7.7. The characteristic signal of the zerovalent palladium complex appears at room temperature: $\text{Pd}(\text{TPPTS})_n$ $\delta = +23.43$.

In order to produce immediately the palladium (0) complex, NaOH is added after dissolving $\text{Pd}(\text{OAc})_2$ in TPPTS solution. The production of the palladium zero complex and OTPPTS is quantitative and the NMR analysis is in accordance with Refs. [14–16].

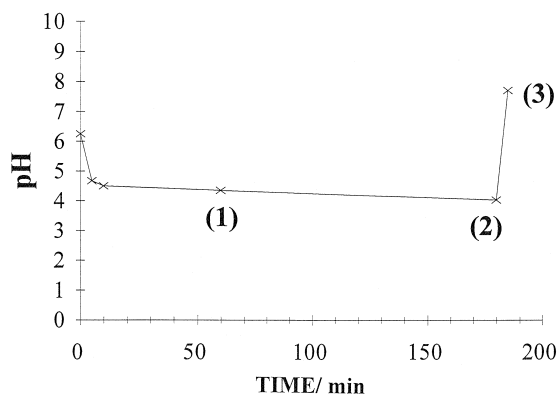


Fig. 2. pH variation as a function of time of the $\text{Pd}(\text{OAc})_2$ –TPPTS system. $[\text{Pd}(\text{OAc})_2] = 4.4 \times 10^{-2} \text{ M}$ and $[\text{TPPTS}] = 0.170 \text{ M}$. (1) and (2): sampling for ^{31}P -NMR spectra. (3): After fast addition of 0.4 M NaOH.

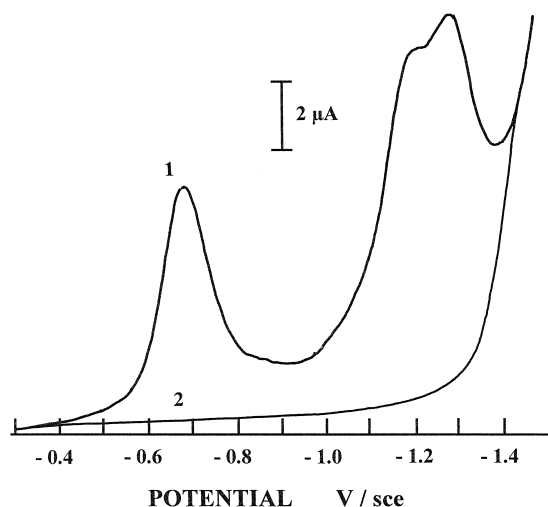


Fig. 3. DPP curve for Pd(OAc)₂-TPPTS system. (1) [Pd(OAc)₂]=3.4×10⁻⁴ M, [TPPTS]=1.5×10⁻³ M. (2) After NaOH addition: [NaOH]/[Pd(OAc)₂]=2.

The electroanalytical study of the Pd(OAc)₂-TPPTS system was also undertaken. A more complex curve was recorded using DPP, since three peaks were observed (Fig. 3). The first one was well-shaped, at -0.7 V/SCE. The two other peaks at -1.2 and -1.3 V/SCE were coalescent. The large potential difference between the first and the two other peaks suggested that three complexes were present, the structures of which being very close for the second and the third. These peaks were decreasing slowly with time, and disappeared completely after a stoichiometric addition of sodium hydroxide (molar ratio NaOH/Pd = 2). We observed that the pH was decreasing from 6.4 to 3.95 in about 3 h before the NaOH addition.

This reduction peak was previously described by AMATORE et al. [19] in acetonitrile-water medium. The slight peak potential difference may be attributed to the presence of acetonitrile (-0.835 V/SCE).

In controlling the pH of the system we have been able to achieve a rapid production of the zero-valent palladium complex. The reduction of Pd(OAc)₂ takes place in a slightly more acidic medium than for PtCl₂. However, the mechanism of this reaction is not obvious because the oxidized state species are not identified. Experiments have been carried out in a sulphuric acid medium (0.24 M and 0.87 M), with a lower TPPTS/Pd ratio so as to limit exchange phenomena during NMR

Table 2

³¹P-NMR spectroscopic data for the Pd(OAc)₂-TPPTS system in H₂SO₄ solutions

Pd(OAc) ₂ concentration (mol/l)	TPPTS/Pd(OAc) ₂	H ₂ SO ₄ (mol/l)	Reaction time	OTPPTS/Pd ^c	δ ppm observed peaks
5.8×10 ⁻²	2.70	0.87	4h	36%	+23.40 ^a + 24.38 + 27.22 + 34.54 + 35.51 + 36.91 ^b
6.0×10 ⁻²	2.48	0.24	8h30	47%	+23.69 ^a + 24.86 ^b + 25.46 + 35.14 + 36.05 ^b

Conditions: Pd(OAc)₂ is dissolved in a TPPTS-H₂SO₄ water solution under argon at room temperature ³¹P NMR measurement at 20°C.

^aProbably Pd(TPPTS)₃.

^bPreponderent peak.

^cOTPPTS production: OTPPTS/ Pd molar ratio.

Table 3

³¹P-NMR spectroscopic data for the TPPTS–PdSO₄-system and phosphorous percentage calculated from NMR spectra

Species	δ ppm (observed peak)	(A)	(B)	(C)
OTPPTS	+ 35.19	25%	22%	20%
free TPPTS	none	none	none	none
Pd(TPPTS) _n , 2 < n < 3	+ 23.62	75%	67%	26.5%
Unknown species	+ 20.83	—	7%	15%
—	+ 23.07	—	—	6%
—	+ 24.92	—	1.5%	29.5%
—	+ 36.22	—	1.5%	3%

(A) TPPTS/PdSO₄: 3.74 after NaOH addition.(B) TPPTS/PdSO₄: 3.25 after NaOH addition.(C) TPPTS/PdSO₄: 3.41, 7 h after mixing.

analysis. These NMR spectra show a lot of peaks due to the oxidized state of Pd and an incomplete reaction after several hours (Table 2).

The behaviour of PdSO₄ is similar to Pd(OAc)₂. The essential difference is that the initial pH of the mixture is less than 2. The reaction is slow with only 66% conversion after 7 h. The NMR spectrum shows numerous peaks which include OTPPTS and Pd complexes (Table 3C).

2.2.1. Palladium zero complex preparation

Under the same initial conditions, by controlling the pH in the 7.0–7.5 range by the addition of NaOH (NaOH/Pd = 2) the production of the palladium zero complex is quantitative and instantaneous (Table 3A).

Under the same conditions, if the initial ratio of TPPTS to Pd is less than 3.5, the reduction of Pd(II) is partial (85% for an initial TPPTS/Pd ratio = 3.25). The NMR spectrum shows the peaks due to the oxidized state (Table 3B).

This phenomenon occurs whatever the operating conditions are (heating, excess of NaOH...) and with Pd(OAc)₂. In our opinion, during the reaction the TPPTS is preferentially complexed by palladium zero. This equilibrium probably limits the concentration of Pd(II) species responsible for the oxido-reduction reaction.

2.3. Rh₂(SO₄)₃–TPPTS

At room temperature the system Rh₂(SO₄)₃–4TPPTS is very stable at pH = 2.3. After 8 h the pH remains unchanged. NMR analysis shows the absence of the oxidation of TPPTS and we can also notice that NaOH causes the precipitation of rhodium hydroxide at pH = 4.3 without OTPPTS production.

This sample shows the limits of the complexing properties of TPPTS. Its poor basicity prohibits its reaction with highly charged cations. Back donation also appears improbable: the filled d-orbitals of Rh(III) are too contracted by the electric charge of the cation to allow bonding with the σ*-orbitals of the phosphorus system.

2.4. RhCl₃–TPPTS

As with the PdSO₄–TPPTS system, the initial pH of the RhCl₃–TPPTS system is acidic but the complexation of Rh(III) by TPPTS is not observed by NMR analysis. In an acidic medium this system

has already been studied in detail [8,11]. The oxido-reduction process is very slow. We have found similar results:

initial TPPTS/RhCl₃ ratio = 5.14:20% oxidation after 5 h,

initial TPPTS/KCl/RhCl₃ ratio = 4/7/1:5% oxidation after 5 h.

The addition of NaOH to the TPPTS–RhCl₃ system provokes an acceleration of the oxido-reduction. However if the pH is maintained at 7.2 the reaction is not quantitative:

OTPPTS/Rh = 0.56 in 1 h, initial TPPTS/RhCl₃ ratio = 3.76,

OTPPTS/Rh = 0.70 in 1 h, initial TPPTS/RhCl₃ ratio = 6.81.

The further addition of NaOH in order to obtain a pH > 10 allows a quantitative reaction (OTPPTS/Rh = 0.96).

For the TPPTS/RhCl₃ system the polarogram recorded was too complicated for analysis. It was obvious that a reduction had occurred, but no peak emerged significantly from the reduction current which could be assimilated to a 'large background'. As previously observed, the addition of sodium hydroxide consequently lowered this current.

The interpretation of the NMR spectrum is more difficult than that of palladium zero and platinum zero because the counter ion of Rh⁺ can change or dissociate.

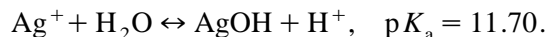
In this system 3 species can be at equilibrium: (TPPTS)₃RhCl, (TPPTS)₃Rh⁺ and (TPPTS)₃RhOH.

Our NMR spectrum of the solution at pH 7.2 (Table 4) is attributed to RhCl(TPPTS)₃ in accordance with previous results [8,22,14,23,15,16]. It is necessary to consider the NMR peak of OTPPTS as a supplementary reference. At pH = 7.2 the multiplet signal of the rhodium system is always near the OTPPTS peak $\Delta\delta = 0.21$ ppm ($\Delta\delta = \delta_{\text{rhodium complex}} - \delta_{\text{OTPTS}}$).

The NMR spectra of the basic solution show a slight but indisputable modification: $\Delta\delta = 1.535$. The preceding system brought to pH 7.2 gives again $\Delta\delta = 0.20$ ppm. The addition of chloride ([Cl⁻]/[Rh] = 10) gives a very similar spectrum.

Our results in basic media do not agree with the spectrum of the isolated complex RhOH(TPPTS)₃ precendently published $\delta = 35.20$, $\Delta\delta = 0.10$ [22,23], the NMR spectrum of which is only slightly different from that of the complex RhCl(TPPTS)₃.

Thus, it is very probable that the hydrolysis of the cation Rh⁺(TPPTS)₃ only occurs in a basic medium which is the case for example for the Ag⁺ cation [24]:



Studies are in progress to measure the basicity of RhOH(TPPTS)₃ in the absence of complexing anions such as Cl⁻.

Table 4

³¹P-NMR spectroscopic data for the rhodium(I)–TPPTS complexes prepared from RhCl₃–TPPTS system

	δ ppm	$\delta(\text{OTPPTS})$	$\Delta\delta$	$J(\text{Rh}, \text{P})$ (Hz)	$J(\text{P}, \text{P})$ (Hz)
pH = 7.2 ^a	+ 35.407	+ 35.197	0.210	143	41
pH = 13 ^b	+ 36.730	+ 35.195	1.535	144	39
pH = 7.2 ^{c,d}	+ 35.397	+ 35.195	0.202	144	39

$\Delta\delta = \delta$ (rhodium complex) – δ (OTPPTS).

^aRhCl₃ = 8 × 10⁻³ M, initial ratio TPPTS/RhCl₃ = 4.3, NaOH/Rh = 2.57, pH = 7.2.

^bNaOH in excess, pH 13.

^cPreceding solution brought to pH 7.2.

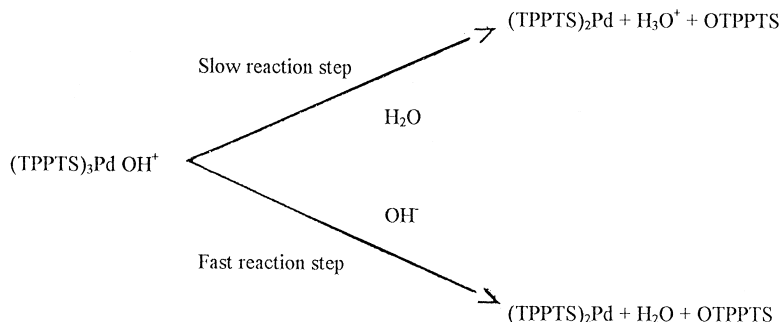
^dAddition of KCl (KCl/Rh = 10) does not perturb the spectrum.

3. Conclusion: Mechanistic considerations

With the Pt(II) and Pd(II) systems, the hydroxide ion reacts in two ways in the fast oxido-reduction reaction. One way is to maximise the concentration of the hydroxo species, as shown in the following example for Pd(II):



The second way is to accelerate the dismutation of the hydroxo complex to OTPPTS and Pd zero by a simultaneous elimination of a proton, (L = TPPTS):



The hypothesis that the hydroxide ion assists the reorganisation of the complex appears probable since in an acidic medium without a complexing anion the Pd(II) is highly hydrolysed and quantitatively complexed by TPPTS. However, these hydrolysed species, while present in large quantities do not disproportionate quickly. Only a more basic medium allows a fast reaction: pH > 5 for Pd(II) and pH > 7 for Pt(II).

At room temperature, the reactivity of the RhCl₃-TPPTS system possesses two particularities:

- The lack of Rh(III) complexation, contrary to Pd(II) and Pt(II), implies that the different hydroxo-chloro Rh(III) species react directly with TPPTS to produce OTPPTS and Rh(I) which is subsequently complexed by the excess of TPPTS.
- With a conversion rate greater than 70% a [Cl⁻]/[Rh(III)] ratio greater than 10 probably provokes the formation of species such as RhCl₄⁻, β₄ = 7.6 or RhCl₅²⁻, β₅ = 8.1 [24] leading to the stopping of the reaction at pH 7. The increase of OH⁻ pH > 10 is necessary to complete the reaction. The β₄ and β₅ constants are not so high as to suppress the hydrolysis and therefore the oxido-reduction.

4. Experimental details

4.1. Equipment

³¹P-NMR spectra were recorded on a Bruker AM 300 (121.51 MHz) and a Bruker AM 200 (81.015 MHz) external reference H₃PO₄ 85%.

pH measurements were performed with a PHN 330 T pH meter (Tacussel, France) and a combined glass electrode.

Polarographic curves were recorded with a 174 PAR Polarograph (EGG, USA) associated with a LY recorder (Linseis, Germany). The working electrode was a dropping mercury electrode (drop time 2 s), the reference was a saturated calomel electrode (SCE), and the auxiliary was a platinum wire.

All experiments were performed under inert atmosphere using argon. The oxygen control in water was measured with a Bioblock Scientific 9071 oxymeter (Bioblock, France) and found to be always less than 0.1 ppm.

4.2. Materials

All reagents were used as supplied by the manufacturers PtCl_2 , $\text{Pd}(\text{OAc})_2$, PdSO_4 , RhCl_3 hydrate, $\text{Rh}_2(\text{SO}_4)_3$ solution... (Aldrich), HClO_4 , H_2SO_4 , NaOH , NaCl ... (Laurylab). TPPTS was prepared by sulfonation of triphenylphosphine, OTPPTS content 1.6% [2].

4.3. General procedures

A 20 ml Schlenk tube is equipped with a pH electrode in an atmosphere of argon. An aqueous TPPTS solution is stirred using a magnetic stirrer.

The initial pH of the aqueous solution was between 6.2 and 7. The solution is deoxygenated by passing argon through it for half an hour. The metallic salt is then introduced into the Schlenk tube. Normally, the experiments were carried out at room temperature except with PtCl_2 which dissolves slowly at 60°C. When the experiments called for the addition of reagents (e.g., NaCl , H_2SO_4 , NaOH ...) these reagents were introduced in solution before the addition of the metallic salt. The initial pH of these experiments are given in Table 1. The deoxygenated NaOH aqueous solution (0.1 M–0.5 M) is added using a syringe. The oxidation of TPPTS by the metallic salt produces an increase in acidity which is progressively neutralised by NaOH . For polarographic analysis, 0.4 ml of the Schlenk tube content was carefully transferred with a syringe and introduced immediately in 50 ml 0.1 M NaNO_3 , previously deoxygenated with argon. For ^{31}P -NMR analysis, D_2O is introduced in the Schlenk tube or in a NMR tube (concentration 20% to 30% in volume).

4.4. PtCl_2 -TPPTS

4.4.1. PtCl_2 -TPPTS

According to the procedure 3.3, 2.05 ml of water containing 3.52×10^{-4} mol of TPPTS are introduced followed by 1.14×10^{-4} mol of PtCl_2 (TPPTS/Pt = 3.08).

After cooling to room temperature the pH is 3.50. 0.2 ml of the solution are taken out for NMR analysis. A very small oxidation to OTPPTS is noticed (2%). The $\text{PtCl}_2(\text{TPPTS})_2$ already identified, appears [3,10] $\delta = +13.9$, $J(\text{Pt}, \text{P}) = 3735$ Hz. Another major but non-identified complex is also observed ($\delta = 24.37$, $J(\text{Pt}, \text{P}) = 2594$ Hz). $\text{Pt}(\text{TPPTS})_n$ is not observed.

4.4.2. PtCl_2 -TPPTS-KCl, 0.37 M

According to the procedure 3.3, 2.05 ml of water containing 0.37 M KCl and 3.06×10^{-4} mol of TPPTS are introduced followed by 7.67×10^{-5} mol of PtCl_2 giving a molar ratio of TPPTS/KCl/ PtCl_2 :4/10/1. After dissolving under the same conditions the final pH is 6.63. NMR analysis shows the absence of the production of OTPPTS. The NMR spectrum is similar to the preceding results with the major non-identified complex.

4.4.3. $Pt(TPPTS)_n$ preparation

After proceeding as for experiment 4.4.1, 0.4 M NaOH is added. On adding 0.1 ml of NaOH the pH rises to 10. After 3 min the pH falls back down to 7.4. The addition of a further 0.1 ml of NaOH causes the pH to rise to 9.84. After 3 min the pH falls back down to 7.9 and so on. The total volume of NaOH added is 0.55 ml. The NMR analysis is in accordance with Refs. [14–16]. The production of the Pt zero complex is quantitative. Note the absence of free TPPTS.

Refs. [14–16]:

$$\delta = +22.20, \quad J(P, P) = 20 \text{ Hz}, \quad J(Pt, P) = 2853 \text{ Hz at } 5^\circ\text{C},$$

$$\delta = +24.10, \quad J(Pt, P) = 2210 \text{ Hz},$$

$$OTPPTS \delta = +34.60.$$

Our results:

$$\delta = +22.90, \quad J(P, P) = 20 \text{ Hz}, \quad J(Pt, P) = 2846 \text{ Hz at } 20^\circ\text{C},$$

$$\delta = +24.80, \quad J(Pt, P) = 2220 \text{ Hz},$$

$$OTPPTS \delta = +35.14.$$

Another experiment with an initial TPPTS/ $PtCl_2$ ratio of 4.2 gives the same results. The NMR spectra are similar with a final TPPTS/Pt ratio between 2 and 4.

4.5. $Pd(OAc)_2$ -TPPTS

4.5.1. $Pd(OAc)_2$ -TPPTS initially without NaOH

According to the procedure 3.3, 0.75 ml of D_2O and 2.32 ml of water containing 5.22×10^{-4} mol of TPPTS (pH = 6.25) are introduced, followed by 1.35×10^{-4} mol of $Pd(OAc)_2$ (TPPTS/Pd = 3.87).

The pH is recorded over time (Fig. 2). Over 5 min the pH drops to 4.67 then changes slowly (pH = 4.03 after 3 h). NMR spectroscopy was performed on the solution 1 h 30 and 3 h after mixing. Numerous peaks appear (8 of which 3 are major)

$$\delta = +35.09 \text{ (OTPPTS)}, \quad \delta = +29.93, \quad \delta = +13.12 \text{ (1 h 30)}, \quad \delta = +17.6 \text{ (3 h)}.$$

After 3 h of reaction time and after having taken the sample for NMR analysis, 2.7×10^{-4} mol 0.4 NaOH are added over a short time. The pH stabilised at 7.7. The production of the palladium(0) complex is quantitative:

$$OTPPTS \delta = +35.10, \quad OTPPTS/Pd = 1.19,$$

$$Pd(TPPTS)_n \delta = +23.03, \quad TPPTS/Pd = 2.87,$$

free TPPTS: none.

The intermediate species have disappeared. A slight overproduction of TPPTS is observed.

4.5.2. $Pd(TPPTS)_n$ preparation

According to the procedure 3.3, 1.5 ml of D_2O and 6.5 ml of water containing 7.85×10^{-4} mol of TPPTS (pH = 6.6) are introduced followed by 2.03×10^{-4} mol of $Pd(OAc)_2$ (TPPTS/Pd = 3.87).

The pH goes down, then 3.86×10^{-4} mol of 0.23 M NaOH are added over a short time to stabilise the pH at 7.4.

The production of the palladium(0) complex is quantitative.

$$\text{OTPPTS } \delta = +35.10, \quad \text{OTPPTS/Pd} = 0.93,$$

$$\text{Pd(TPPTS)}_n \delta = +23.60, \quad \text{TPPTS/Pd} = 2.87,$$

free TPPTS: none.

4.6. PdSO₄–TPPTS

4.6.1. TPPTS / Pd > 3.5: Pd(TPPTS)_n preparation

According to the procedure 3.3, 2.35 ml of water containing 5.16×10^{-4} mol of TPPTS (pH = 6.23) are introduced followed by $1.38 \cdot 10^{-4}$ mol of PdSO₄ (TPPTS/Pd = 3.74).

(pH = 1.93). Over 20 min 2.96×10^{-4} mol of 0.4 M NaOH are added [pH = 7.86 NaOH/Pd = 2.1].

The palladium(0) complex is quantitatively produced:

$$\text{OTPPTS } \delta = +35.19, \quad \text{OTPPTS/Pd} = 0.97,$$

$$\text{Pd(TPPTS)}_n \delta = +23.62, \quad \text{OTPPTS/Pd} = 2.74.$$

(Table 3A).

4.6.2. TPPTS / Pd < 3.5

The previous procedure is used, but with a lower ratio: TPPTS/Pd = 3.25. The pH is stabilised at 7.4 with 0.4 M NaOH (NaOH/Pd = 1.90).

The NMR spectrum of the aqueous solution exhibited 5 signals (Table 3B). The reduction is not quantitative, the spectrum does not change after heating the solution for 1 h (85% of Pd(II) is reduced).

4.6.3. Without NaOH

Following the procedure 3.3, 2.5 ml of water containing 4.48×10^{-4} mol of TPPTS (pH = 6.40) are introduced, followed by 1.31×10^{-4} mol of PdSO₄ (initial pH = 2.24). The pH falls down to 2. Seven hours later the NMR spectrum in the aqueous solution also exhibited 6 signals (Table 3C). The reduction is not quantitative.

4.7. Rh₂(SO₄)₃–TPPTS

According to the procedure 3.3, 1.5 ml of water containing 3.28×10^{-4} mol of TPPTS and 0.106 g of an acidic water solution of Rh₂(SO₄)₃ containing 7.8×10^{-4} mol of rhodium sulfate are introduced (TPPTS/Rh = 4.2). The pH is stabilised at 2.29. Eight hours after mixing, the NMR spectrum of the solution is identical to that of TPPTS alone ($\delta = -5.27$) without OTPPTS production.

The addition of 8×10^{-4} mol of 0.19 M NaOH causes the precipitation of Rh(OH)₃ at pH = 4.3 without OTPPTS production.

4.8. RhCl₃–TPPTS

4.8.1. Without NaOH

According to the procedure 3.3, 3 ml of water containing 4.8×10^{-4} mol of TPPTS are introduced, followed by 9.33×10^{-5} mol of RhCl₃ (TPPTS/RhCl₃ = 5.14).

After 5 h the NMR spectrum of the aqueous solution exhibits OTPPTS and a rhodium complex peak near the OTPPTS peak:

$$\text{OTPPTS } \delta = +35.08, \quad \text{OTPPTS/Rh} \cong 20\% - 25\%,$$

$$\text{Rh complex } \delta = +35.40, \quad J(\text{Rh}, \text{P}) = 143 \text{ Hz}, J(\text{P}, \text{P}) = 40 \text{ Hz}.$$

4.8.2. With KCl

According to the procedure 3.3, 3 ml of water containing 3.0×10^{-4} mol of TPPTS and 5.25×10^{-4} mol of KCl are introduced, followed by 7.5×10^{-5} mol of RhCl_3 (TPPTS/KCl/Rh = 4/7/1), pH = 2.15.

After 7 h the NMR spectrum of the aqueous solution shows the presence of a rhodium complex 5% near to the OTPPTS peak.

Then 1.3×10^{-4} mol of 0.24 M NaOH are added over 45 min. The pH is 9.04.

The NMR spectrum of the aqueous solution exhibits:

$$\text{OTPPTS } \delta = +35.14, \quad \text{OTPPTS/Rh} = 60\%,$$

$$\text{Rh complex } \delta = +35.46, \quad J(\text{Rh}, \text{P}) = 142 \text{ Hz}, \quad J(\text{P}, \text{P}) = 39 \text{ Hz}.$$

OTPPTS production is not quantitative (60%).

4.8.3. With NaOH

According to the procedure 3.3, 5.5 ml of water containing 2.05×10^{-4} mol of TPPTS (pH = 7.6) are introduced, followed by 4.43×10^{-5} mol of RhCl_3 (TPPTS/Rh = 4.63), pH = 2.2. In 2 h 1.14×10^{-4} mol of 0.19 M NaOH are added, pH = 7.2. (NaOH/Rh = 2.57.)

The NMR spectrum of the aqueous solution shows the presence of a rhodium complex with a non-quantitative OTPPTS production.

$$\text{OTPPTS } \delta = +35.14, \quad \text{OTPPTS/Rh} = 0.63,$$

$$\text{CIRh(TPPTS)}_n \delta = +35.39, \quad J(\text{Rh}, \text{P}) = 143 \text{ Hz}, \quad J(\text{P}, \text{P}) = 41 \text{ Hz}.$$

Then 0.9×10^{-4} mol of NaOH are added pH > 11. The NMR spectrum of the aqueous solution exhibits a quantitative OTPPTS production and a shift of the peak (quadruplet).

$$\text{OTPPTS } \delta = +35.14, \quad \text{OTPPTS/Rh} = 1.02,$$

$$\delta = +36.53, \quad J(\text{Rh}, \text{P}) = 151 \text{ Hz}, \quad J(\text{P}, \text{P}) = 38 \text{ Hz}.$$

Then 0.645 ml of 0.44M H_2SO_4 are added. The NMR spectrum of the aqueous solution exhibits again the first complex

$$\text{OTPPTS } \delta = +35.19,$$

$$\text{CIRh(TPPTS)}_n \delta = +35.36, \quad J(\text{Rh}, \text{P}) = 144 \text{ Hz}, \quad J(\text{P}, \text{P}) = 40 \text{ Hz}.$$

The same spectra are obtained with initial ratios TPPTS/Rh = 6.8 and 4.

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