

Nickel(0)-TPPTS-Cyanide Complex in Water

An Efficient and Flexible Catalyst for the Isomerisation of Olefinic Compounds at Room Temperature

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Résumé — Complexe de nickel(0)-TPPTS-cyanure dans l'eau. Un catalyseur efficace et flexible pour l'isomérisation des composés oléfiniques à température ambiante — Depuis 30 ans, la TPPTS a permis le développement de systèmes biphasés eau-organique pour de nouveaux procédés « verts » offrant une séparation aisée du catalyseur. Cependant, les réactions d'isomérisation des oléfines au moyen de complexes de phosphore ou de phosphine de nickel connues en milieu organique ne peuvent être aisément transposées en système biphasé eau-organique, car le complexe de Ni(0)-TPPTS n'est pas suffisamment stable en milieu aqueux. Pour y parvenir, nous avons stabilisé le complexe de Ni(0)-TPPTS avec un ligand cyanure en milieu basique. Un tel système biphasé Ni(0)-TPPTS-cyanure montre une forte activité catalytique pour l'isomérisation des butènes et autres oléfines à température ambiante avec une séparation du catalyseur aisée.

Abstract — Nickel(0)-TPPTS-Cyanide Complex in Water. An Efficient and Flexible Catalyst for the Isomerisation of Olefinic Compounds at Room Temperature — For the past 30 years, the TPPTS synthesis has allowed the development of water-organic biphasic systems offering new green processes with an easy catalyst separation. However, olefin isomerisation reactions based on nickel phosphite or phosphine complexes in organic media cannot be easily adapted in a water-organic biphasic system because the Ni(0)-TPPTS complex is not stable enough in an aqueous medium. To make this adaptation successful, we stabilized the Ni(0)-TPPTS complex with cyanide ligands in basic medium. Such a biphasic Ni(0)-TPPTS-cyanide system revealed a high catalytic activity for the isomerisation of butenes and other olefins at room temperature with a simple catalyst separation.

INTRODUCTION

Since the synthesis of the trisodium salt of tri(*m*-sulphophenyl) phosphine (TPPTS, *Fig. 1*) in 1974, the organometallic catalysis in water has been widely developed as well in industry as in university [1-3]. The hydrosoluble system Rh-TPPTS is the catalyst of the most famous industrialised reaction in the field of biphasic catalysis: the hydroformylation of propene into *n*-butanal by the *Ruhrchemie-Rhône-Poulenc* process. The same rhodium system is also used in the industrial synthesis of geranylacetone, an intermediate for vitamin E, by the Rhône-Poulenc Animal Nutrition process. The excellent regioselectivity, the easy recovery and the recycling of the aqueous rhodium catalyst permit the industrialisation to produce geranylacetone in a short and economical process compared to the old chemistry which used linalool, a more expensive raw material [4-6].

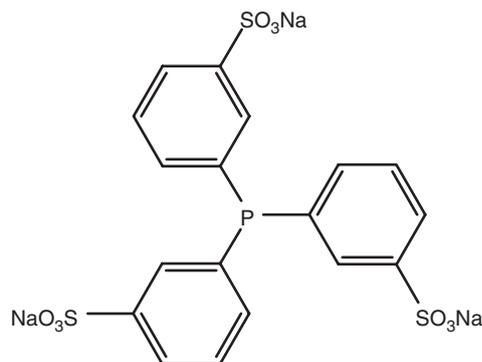


Figure 1

TPPTS: trisodium salt of tri(*m*-sulphophenyl) phosphine.

The *Ruhrchemie-Rhône-Poulenc* process constituted, according to R.A. Sheldon's classification (University of Delft, the Netherlands), a fundamental advance in three areas: environment, conservation of resources and minimization of pollution. R.A. Sheldon defined the environmental factor E as essentially being the relation between the amount of by-product manufactured per kilogram of useful product produced. The factor E varies from 0.1 in refining to 1-5 in basic chemistry, up to 5-50 in fine chemistry and 25-100 in pharmaceutical industry [7]. This factor for a biphasic hydroformylation process is estimated at 0.04, *i.e.* ten times lower than for all the other known hydroformylation processes. Moreover, the "immobilisation" of the hydrosoluble Rh-TPPTS catalyst in the aqueous phase led to a loss in rhodium over ten years lower than 2 kg for 2 million tons of *n*-butanal produced. Over these ten years, the controlled use of this noble metal was achieved in a large amount of water. Thus, the biphasic *Ruhrchemie-Rhône-Poulenc* process is both a green process and a highly cost-effective process [8].

Although biphasic systems with water are extremely attractive for their easy catalyst separation, the development of industrial processes based on has been considered so far only with precious metals [1]. However, an other way of biphasic catalysis with nickel and based on liquid imidazolium salts was started by Yves Chauvin at IFP. The use of those salts in biphasic catalysis has known a large interest in academic and industrial laboratories [9, 10].

In fact, TPPTS complexes with non precious metals such as iron, cobalt, nickel and copper have been found too unstable in water for practical uses. Nevertheless, in the seventies water soluble nickel(0)-TPPTS complexes were discovered and used as catalysts in water for butadiene and olefin hydrocyanation [11] and diene telomerisation [5].

More recently, by using the sodium salt of tetra-sulphonated 1,4-bis(diphenylphosphino)butane and nickel salts, olefins or allylic alcohols were isomerised in a biphasic system in acidic media [12, 13]. The best initial turnover frequency (TOF: mole of isomerised olefin per mole of catalyst per hour) was only 106 h⁻¹ with a turnover number (TON: mole of isomerised olefin per mole of catalyst) of 50. In these conditions, the Ni(0)-TPPTS system is unfortunately not stable enough at 80°C and an excess of TPPTS does not entirely prevent the decomposition of the nickel complex into Ni²⁺ and hydrogen. It is therefore not possible to replace the isomerisation of olefins as it has been reported with phosphite or phosphine complexes in organic acidic media [14, 15] by the biphasic Ni(0)-TPPTS system as such.

In order to adapt such isomerisation reactions into a promising biphasic system, we studied the potential of the biphasic Ni(0)-TPPTS system in presence of cyanide for the isomerisation of olefinic compounds.

1 RESULTS AND DISCUSSION

³¹P NMR spectroscopic and polarographic studies of Ni(TPPTS)_n-TPPTS-NaCN aqueous solutions in basic media (pH = 11-12) show the appearance of stable nickel zero complexes: chemical shift of [Ni(TPPTS)₃CN]⁻ δ = +29.9; [Ni(TPPTS)₂(CN)₂]²⁻ δ = +29.3; Ni(TPPTS)₃ δ = +23.3 and TPPTS δ = -5.6. At pH 7-8 the system (CN⁻/Ni < 2) was slightly unstable leading to hydrogen release and nickel (Ni²⁺) formation. No evidence of the active species, the nickel hydride complexes, has been found by ¹H NMR. If present, they should be formed in very small quantity. An excess of sodium cyanide yields free TPPTS and a very unstable nickel zero cyanide complex which is quickly oxidized into the well-known nickel tetracyanide complex [Ni(CN)₄]²⁻ observed by polarography (reduction at -1.6 volt/SCE - saturated calomel reference). However, there is a pH range between 8 and 11 in which the system could be stable enough to generate a nickel hydride allowing a catalytic reaction. The use of sodium borohydride to reduce

Ni^{2+} allows to stabilize the pH around 9.5 through borate formation. The catalytic system was then prepared by the addition of sodium borohydride to a deoxygenated aqueous solution of NiSO_4 -TPPTS- NaCN at different ratios under argon atmosphere [16, 17].

At room temperature the catalytic system is very efficient: 2.5 mL of aqueous phase containing the catalyst (and 2.5 mL of ethanol to obtain a perfect decantation) converted 3 mL of eugenol (**1**) into isoeugenol (**2**) [conversion 94% (6 min), 99% (15 min)]. The initial TOF was 1800 h^{-1} and the initial isoeugenol trans-cis ratio (92-8) evolved towards the thermodynamic equilibrium (95-5) (Fig. 2).

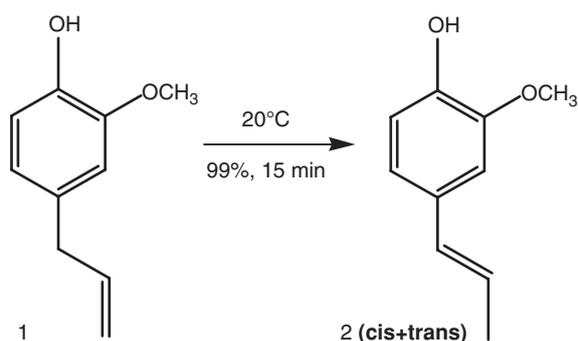


Figure 2

Eugenol isomerisation at RT.

Reagents: volume ratio of water/ethanol/eugenol: 2.5/2.5/3, molar ratio of NiSO_4 /TPPTS/ NaCN / NaBH_4 /eugenol: 1/4/2/1.2/195.

In similar conditions, the allylbenzene (**3**) was isomerised into propenylbenzene (cis+trans) (**4**) (Fig. 3). The hydrocyanation of allylbenzene in 4-phenylbutyronitrile (**5**) was also observed as a minor side reaction.

The main factor that controls the activity of the catalyst is the initial molar ratio $\text{NaCN}/\text{NiSO}_4$ (Table 1). With a molar ratio equal to 0.94, the reaction is highly selective for isomerisation (99.9%). Only 0.1% of hydrocyanation occurs, *i.e.* only 7% of the cyanide introduced is converted to 4-phenylbutyronitrile. With a ratio equal to 2, 4-phenylbutyronitrile appears preferentially within the first minutes, then the reaction becomes selective for isomerisation. With a molar ratio equal to 8, the olefin conversion is low and 4-phenylbutyronitrile is the major product. It is therefore tentative to conclude that the monocyano complex selectively catalyses the isomerisation and the dicyano complex the hydrocyanation side reaction in our conditions.

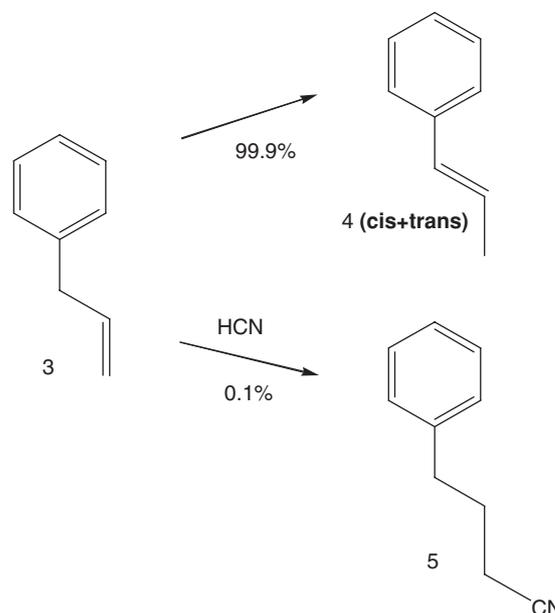


Figure 3

Allylbenzene isomerisation at RT.

Reagents: volume ratio of water/ethanol/allylbenzene: 2.5/1.2/1, molar ratio of NiSO_4 /TPPTS/ NaCN / NaBH_4 /allylbenzene: 1/4/x/1.2/75.

TABLE 1
Allylbenzene reactivity

NaCN/Ni molar ratio (x)	Reaction time (%)	Olefin conversion (%)	Isomerisation selectivity (%)	Hydrocyanation selectivity (%)
0.94	2 h	99	99.9	0.1
2	5 min	1.5	40	60
	18 h	98	98.5	1.5
8	2 h	5	23	77
	17 h	10	28	70

The optimum pH value is around 9.5. In a more basic medium, $\text{pH} > 11$, no reaction occurs. In more acidic conditions, the catalyst system is less stable and inactive Ni^{2+} complexes appears. No nickel was detected in the organic phase ($< 1 \text{ ppm}$).

The 1-butene gas was isomerised with the same catalytic system at atmospheric pressure and room temperature but with a lower TOF (24 h^{-1}). The catalytic system always leads to a mixture of butenes at the thermodynamic equilibrium composition: 1-butene (5%), *cis*-2-butene (22%), *trans*-2-butene (73%).

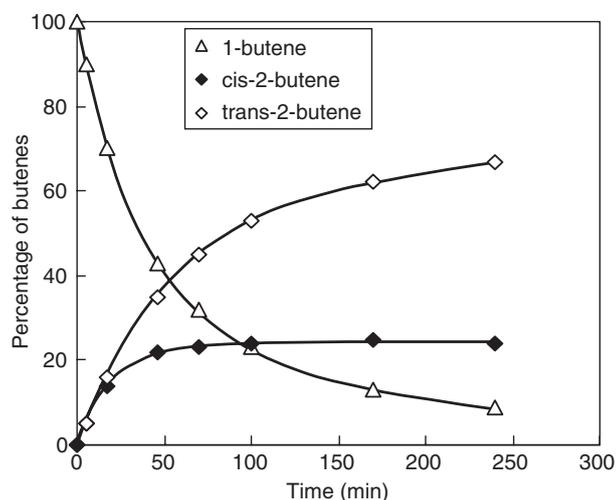


Figure 4

Kinetics of 1-butene isomerisation at RT.

Reagents: volume ratio of water/ethanol/1-butene: 2/2/12, molar ratio of NiSO_4 /TPPTS/ NaCN / NaBH_4 /1-butene: 1/3.6/1.2/3/1500.

The 1-butene isomerisation was also carried out in biphasic water - liquid olefin conditions in a glass reactor (RT, initial pressure of 1-butene 1.8 bar, final pressure of butenes 1.3 bar). The initial TOF was 264 h^{-1} . The addition of ethanol accelerated the reaction with an initial TOF of 780 h^{-1} . A kinetic effect was also observed in the first minutes: the *cis/trans*-2-butene ratio initially equal to 1, reached 0.3 at the thermodynamic equilibrium. The TON is 1400, which demonstrates an acceptable stability of the catalytic system (Fig. 4).

When a more water-soluble olefin like 3-buten-1-ol was used, octane was added to limit the concentration of water in the organic phase for accurate chromatographic analyses. In these conditions, 3-buten-1-ol was converted to *trans*-2-buten-1-ol in a few minutes at RT or 0°C (Figs. 5, 6). An initial TOF of 3600 h^{-1} is observed at RT and 1800 h^{-1} at 0°C . The 2-buten-1-ol is transformed to butanal with a lower TOF (300 h^{-1} at RT and 18 h^{-1} at 0°C).

Without cyanide the nickel TPPTS system did not isomerise the olefins in the previous conditions. The addition of cyanide allows a higher electronic density of nickel and therefore the formation of a nickel hydride by reaction with water at pH 9.5. The saturation of the nickel complex with the olefin probably prevents the oxidation of the complex.

In a continuous process, the oxidized form of the catalyst Ni(II)-TPPTS-cyanide resulting from the slow oxidation of the Ni(0) catalyst, should be continuously reduced back to nickel Ni(0) electrolytically as already proposed for the hydrocyanation of olefins by Ni(0) TPPTS complexes [18]. This will increase the life span of the isomerisation catalyst and therefore improve the environmental factor E of the process.

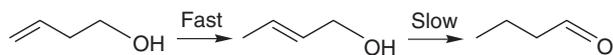


Figure 5

3-buten-1-ol isomerisation.

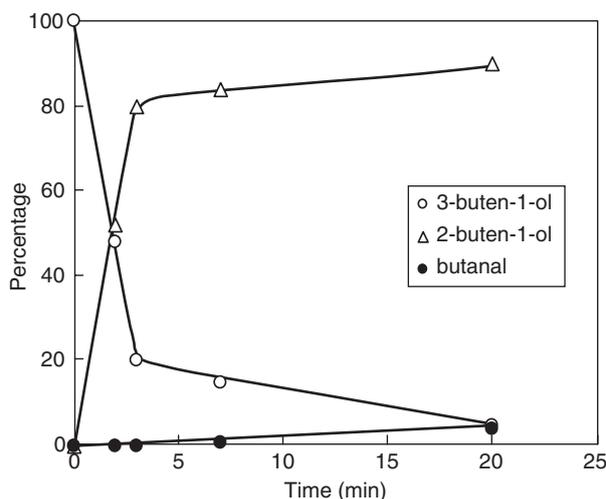


Figure 6

Kinetics of 3-buten-1-ol isomerisation at 0°C .

Reagents: volume ratio of water/octane/3-buten-1-ol: 2/2.6/1.3, molar ratio of NiSO_4 /TPPTS/ NaCN / NaBH_4 /3-buten-1-ol: 1/6/0.95/1.2/150.

2 EXPERIMENTAL

Experiments were carried out under inert atmosphere (argon). In a typical reaction, 2.5 mL of water containing 10^{-4} mole of NiSO_4 (4.10^{-2} M), 3.2 equiv. of TPPTS, 1.0 equiv. of NaCN were put into a 20 mL Schlenk tube with a magnetic stirrer. The system was deoxygenated by flowing under argon for 30 minutes. The olefins were introduced as liquids except 1-butene introduced as gas. Then 0.1 mL of water containing 1.2 equiv. of NaBH_4 was added. The liquid organic phase was analysed over time (or gas phase with 1-butene).

The experiments with liquid butenes at low pressures were performed in a 50 mL glass reactor at 20°C . 1-butene was introduced at atmospheric pressure at -5°C into the reactor which contained the aqueous nickel (II) catalyst system, then sodium borohydride was added and the system was heated at 20°C (initial pressure 1.8 bar). Butenes in equilibrium between the gas phase and the liquid phases (organic and aqueous) were isomerised by the catalyst in the red aqueous phase. The gas phase was analysed over time (final pressure 1.3 bar).

NMR measurements of the Ni-TPPTS system were achieved at -30°C in an ethanol-water- D_2O mixture in presence of NaOH 0.002 M. At room temperature, TPPTS in excess and $\text{Ni}(\text{TPPTS})_3$ cannot be separately observed because of fast TPPTS exchanges. The Ni-TPPTS system concentration in the NMR tube was 0.02 M in nickel with a ratio TPPTS/Ni = 4.2. This aqueous solution of complex was prepared by a ligand exchange of $\text{Ni}(\text{COD})_2$ with TPPTS (0.15 M in nickel pH = 9.2 with a ratio TPPTS/Ni = 4.2) [11, 17]. It was essential to perform the dilution in presence of sodium hydroxide for the addition of reagents to avoid a low decomposition of the complex. In presence of cyanide, no exchange occurred in the system anymore. The system could be studied at RT without ethanol. Sodium cyanide in aqueous solution was added last.

CONCLUSION

Water-soluble Ni(0)-TPPTS-cyanide complexes are efficient as catalysts for the isomerisation of olefins at low temperatures. The 1-butene isomerisation into a mixture of 1-butene and 2-butenes at the thermodynamic equilibrium was carried out with a TON greater than 1000 and with an excellent volumic productivity.

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