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Tetrakis (Hydroxymethyl)Phosphonium Chloride for Crosslinking Polyethylenimine (PEI) to Improve Metal Ion Extraction †

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‡ In memoriam to our friend, the Professor M.A. Didi deceased in traffic accident in Oran (Algeria) on the 17 January 2023.

Abstract

Tetrakis (Hydroxymethyl)Phosphonium chloride (THPC) in aqueous solution reacts with amines to form aminomethylenephosphines. The reaction was studied with piperidine, and THPC was used with PEI. The reaction with PEI leads to new polymers with phosphine groups (PEI-P) and phosphine oxide (PEI-PO) after oxidation by hydrogen peroxide. These polymers coordinate cations of transition metals, lanthanides and actinides.

Keywords: polyethylenimine; PEI; THPC; metal extraction; cross-linking

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1. Introduction

Tetrakis (Hydroxymethyl) Phosphonium chloride (THPC) in aqueous solution was obtained by Alfred Hoffman (1921) by reacting phosphine with hydrochloric formaldehyde solution [1].

$$PH_3 + 4\ HCHO + HCl \longrightarrow {}^{+}P(CH_2OH)_4,\ Cl^{-}$$

Scheme 1. Formation du THPC chloride.

The THPC exist as un equilibrium in water with tris (hydroxymethyl)phosphine (THP), and this equilibrium can easy shift in presence of an basis to THP.

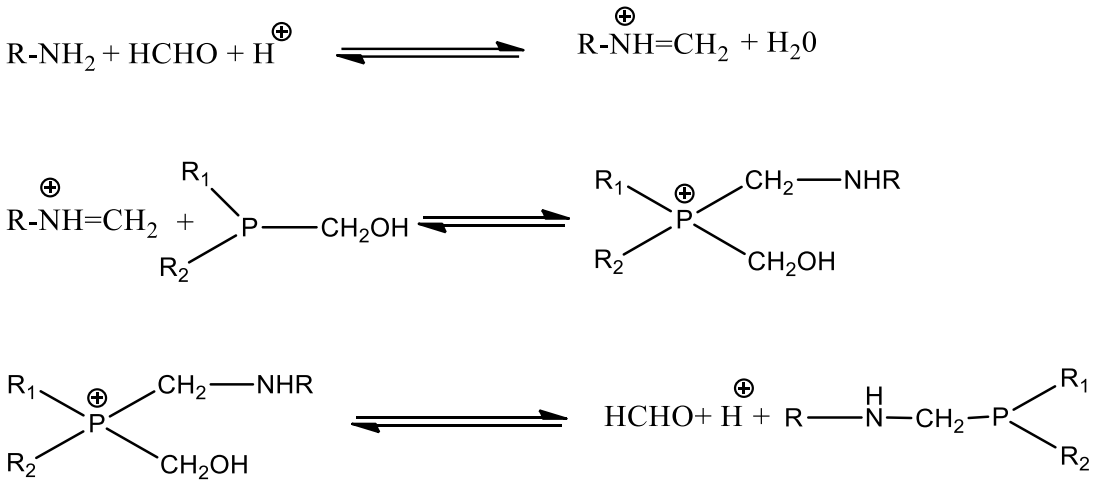
$${}^{+}P(CH_2OH)_4,\ Cl \rightleftharpoons P(CH_2OH)_3 + HCHO + HCl$$

Scheme 2. THPC in water (equilibrium).

THPC is commercially available as a textile flame retardant agent [2]. THPC is a precursor of THP a precursor of aminomethylphosphines used in organometallic chemistry

such as 1,3,5-triaza-7-phosphaadamantane (PTA), a water-soluble ligand of transition metal [3].

The synthesis of aminomethylphosphines is a Mannich reaction catalyzed by a Bronsted acid, so THPC can be used as source of THP and HCl.



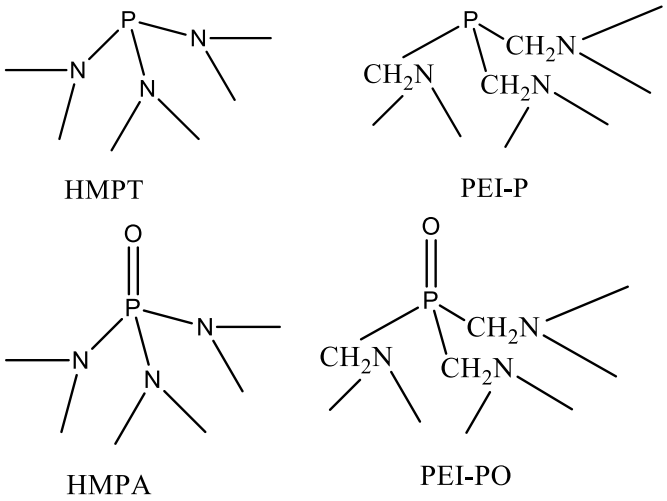
Scheme 3. Mannich condensation of THP with amine.

2. Results and Discussion

During our work on new Suzuki reactions [4], we have studied the formation of new ligand aminomethylphosphine formed by the reaction of THPC with amines.

A model of this reaction was the reaction of piperidine with THPC in the formation of tris (methylenpiperidine) phosphine. This air sensitive phosphine has been characterized by its air stable palladium complex and by oxidation in air stable tris (methylenpiperidine) phosphine oxide.

In general, tris (methyleneamine) phosphines are close to HMPT [5] and their oxide are close to HMPA [6] known to their abilities to coordinate metal ions, with phosphine as soft ligand and phosphine oxide as hard ligand.



Scheme 4. Substructure comparison between PEI-P and HMPT; PEI-PO and HPMPA.

We previously showed that phosphonic PEIs obtained by the Modrizer-Irani reaction (a Mannich type reaction) are metal ion coordinating agents [7]. So we have explored the use of THPC for cross-linking PEI with phosphine and phosphine oxide bridges.

The reaction of THPC with PEI take place easily in aqueous ethanolic solution of PEI under argon in order to obtain phosphine bridges (PEI-P). The reaction was performed with a large game of PEI generously gift by BASF (M = 8, 25, 1000, 2000 kD).

During the reaction of THPC with PEI, the NH_2 groups (ν = 3147 cm^{-1}) disappeared and also new OH groups (ν OH = 3147 cm^{-1}) appeared in infrared spectroscopy.

The ^{31}P NMR show new signals (signals δ= −23.4; −29.4; −33.0 ppm). These are attributed to $NHCH_2P(CH_2OH)_2$, $[NHCH_2]_2$ P CH_2OH (bridge), $[NHCH_2]_3$ P.

The surface measured by BET also diminishes (10.2 m^2g^{-1} from to 2.6 m^2g^{-1}).

All these observation show an incomplete reaction of THPC with cross-linking of PEI and the formation of different phosphine groups (PCH_2OH and $NHCH_2$ P) on the surface of PEI.

The phosphine groups were oxidized with an aqueous solution of hydrogen peroxide to phosphine oxide group (PEI-PO) and has characterize by P=O (ν = 1180 cm^{-1}) vibration in infrared and disappearing phosphine signal and new signals in ^{31}P NMR (signals δ = +24 to +40 ppm) appeared.

The PEI-P rapidly discolored aqueous solution of colored metallic cations (Cu^{+2}, Co^{+2}, Fe^{+3}, Ru^{+3},VO^{2+}, Pd^{+2}) and the PEI -PO discolored Ce^{+4}, UO_2^{+2}, solution.

Quantitative extraction (follow by visible spectrometry in presence of with Arsenazo III) of lanthanides (Sm^{+3}, La^{+3}, Nd^{+3}) and actinides' ($UO_2^{2,}$ $^{Th+3}$) were studied at the LSPT (Tlemcen, Algeria) with PEI-PO prepared at LCMT (Caen, France).

3. Perspectives

The reaction of THPC with PEI allows for numerous applications based on increased metal ion coordination, with cross-linking PEI with increasing the strength of PEI polymers. Potential applications include metal extraction using PEI resins [7] or as a selective membrane [8]. Modification of nanoparticles-PEI [9] as a catalyst or extraction agent is also possible, as is modification of PEI for biological applications [10].

4. Experimental

Equipment:

^{31}P NMR spectra were recorded at 100.6 MHz with ^{1}H decoupling, on a on a Bruker DRX 400 instrument. Chemical shifts are expressed in ppm relative to H_3PO_4. Infrared reflection spectra were recorded on a Perkin-Elmer Spectrum One spectrometer.

4.1. Reaction Model: THPC with Piperidine

4.1.1. Tri (N-Piperidylmethylene)Phosphine

1.36 g (16 mmol, 4 equ) of piperidine is placed in a two-necked flask under argon. The flask was cooled in an ice bath. 952 mg of an aqueous solution of tetrakis (hydroxymethyl) phosphonium chloride (THPC) (4 mmol, 80% aqueous solution) was then slowly added using a syringe. The reaction was highly exothermic and was accompanied by the release of hydrochloric acid. A slightly sticky white solid was obtained, insoluble in water. Any attempt at purification was impossible since the product oxidizes in air and becomes deliquescent. It should therefore be coordinated as soon as it is formed.

$[(CH_2)_5NCH_2]_3P$: RN = 135053-54-2

NMR^{31}P ($CDCl_3$): −62.6 ppm

4.1.2. Tri (N-Piperidylmethylene) Phosphine Oxide

Tri (N-piperidylmethylene) phosphine is dissolved in 10 mL of dichloromethane. 10 mL of 30% hydrogen peroxide was added. The mixture was stirred for a few minutes. The organic phase is collected, dried over magnesium sulfate, filtered, and evaporated. Colorless oil was obtained.

$[(CH_2)_5NCH_2]_3PO$: RN = 2328-96-3

NMR ^{31}P ($CDCl_3$): +50 ppm

4.1.3. Bis (Tri(N-Piperidylmethylene) Phosphine)-Palladium (II) Chloride

355 mg of palladium (II) chloride (2 mmol, 1 equ), dissolved in a minimum of DMF, was added by syringe to tri (N-piperidylmethylene) phosphine (4 mmol, 2 eq) under argon flow. The mixture turns yellow, then a paste forms which agglomerates. After stirring overnight at room temperature, a dark precipitate appears. The precipitate was filtered through a Büchner funnel and washed with ether. 876 mg of a black solid are thus obtained (yield = 53%).

$[(CH_2)_5NCH_2]_3P]_2\ PdCl_2$

NMR ^{31}P (THF-d8): −2.6 pppm

4.2. THPC with PEI

4.2.1. PEI-Phosphine (PEI-P)

Under argon, THPC (14.3 mL or 19.6 g; 0.08 M 9.928 P) in ethanol (20 mL) was added to a solution of water (100 mL) with ethanol (5.4 L) with PEI 25 kD (29 g) (0.045 eqmol). The mixture forms white foam and was refluxed for 2 h, turning to a solution yellow. The solution was evaporated under vacuum at 70 °C, leaving a yellow resin. The pale yellow polymer is washed with water (20 mL) and recovered by centrifugation six times under argon.

- Analysis: 1.7% of P
- IR (ATR powder): 3470 cm^{-1} (OH), 3362 cm^{-1} (large NH); 710–700 cm^{-1} (C-P)
- ^{31}P NMR (H_2O, HCl): δ = −23.4; −29.4; −33.0 ppm

4.2.2. PEI-Phosphine Oxide (TEI-PO)

- IR (ATR powder): 3470 cm^{-1} (OH), 3362 cm^{-1} (large NH); 710–700 cm^{-1} (C-P)
- ^{31}P NMR (H_2O, HCl): δ = −23.4; −29.4; −33.0 ppm
- IR (ATR powder) 3470 cm^{-1} (OH), 3362 cm^{-1} (large NH); 1180 cm^{-1} (P=O).
- ^{31}P NMR (H_2O, HCl): δ = +24 to +40 ppm.

4.3. Preliminary Qualitative Metal Coordination Tests

Aqueous solutions of $NiCl_2$, $CoCl_2$, $FeCl_3$, $RuCl_3$, Na_2PdCl_4, $VOSO_4$, $CeCl_4$, and $UO(C_2H_3O_2)_2$ were stirred in the presence of PEI-P or PEI-PO until discoloration, demonstrating the ability of these resins to coordinate metal cations.

5. Conclusions

The reaction of THPC with PEI allows increased metal ion coordination, PEI-P are particularly good for coordinating transition metal ions and PEI-PO are very good for the coordination of lanthanides and actinides.

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Conflicts of Interest: The authors declare no conflict of interest.

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