

## UNSATURATED PHOSPHONIC ACID, A NOVEL PRECURSOR TO FABRICATE METAL ORGANIC FRAMEWORKS

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### ABSTRACT

Investigations on phosphonates metal organic frameworks (MOFs) have attracted interest during the last two decades due to their captivating network topology, structural flexibility and multiple special properties. The synthesis of 1-phenylphosphonium acid, as precursor of metal organic framework was described. The synthesized compound was analyzed by <sup>1</sup>H and <sup>31</sup>P-NMR, HPLC, MS, TG and IR spectroscopy. The PM3 semi-empirical analysis of precursor was made in order to establish their design, structural properties, thermodynamic and electronic properties.

### INTRODUCTION

The chemistry of organophosphorus compounds was rapidly developed due to the multiple properties that can potentially act. Most of metal organic frameworks exhibit a variety of open framework architectures.<sup>1,2</sup> These compounds received extensive research attention in recent years due to their applications in the areas of gas storage,<sup>3</sup> heterogeneous catalysis,<sup>4</sup> separation,<sup>5</sup> ion exchange,<sup>6</sup> magnetism,<sup>7</sup> sensors,<sup>8</sup> etc. An outstanding class of metalphosphonates is the one that use a phosphonic derivative containing a double bond. Conant<sup>9</sup> describe the synthesis of 1-phenylphosphonic acid PVP in two ways: from acetophenone, phosphorus trichloride and acetic acid or acetophenone, phosphorus trichloride and water at 150°C. High temperature is needed to remove unreacted acetophenone. Chosen method using an excess of acetophenone, to serve as reactant, is advantageous in practical terms. After mixing with phosphorous trichloride with acetophenone, preferably at room temperature, water is added in drops to maintain the reaction mixture between 5-20°C. The reaction mixture contains acid, product and unreacted acetophenone. The acetophenone removal is done by driving under vacuum at temperatures below 100°C.



Acid is separated from the reaction mixture by recrystallization from hydrochloric acid.

### MATERIALS and METHODS

#### *Analysis methods*

PVP acid was characterized by physicochemical methods: mass spectroscopy, NMR spectroscopy, IR spectroscopy, UV-VIS spectroscopy, high performance liquid chromatography (HPLC), thermogravimetric analysis (TG).

#### *Materials*

For synthesis were used acetophenone (Aldrich), phosphorus trichloride (Aldrich), without other purification and distilled water.

*Quantum chemical method*

Gas phase equilibrium geometry of conformers was obtained by semi-empirical PM3-RHF calculations using the Polak-Ribiere conjugate gradient algorithm for geometry optimization<sup>10</sup>. Stop criteria were: SCF convergence of  $10^{-5}$  and RMS gradient of  $10^{-2}$  kcal/A·mol. Calculations have been performed with HyperChem7.52 package<sup>11</sup>.

*Experimental method:*

Into a 500 ml reaction flask filled with nitrogen 2.75 moles acetophenone and 1.82 moles of  $\text{PCl}_3$  were placed and stirred at room temperature for one hour. To the reaction mixture was added dropwise 3.64 moles of distilled water. The reaction temperatures was adjusted with ice at  $5^\circ\text{C}$  to the beginning of the water addition and increased at  $50^\circ\text{C}$  when the addition was completed. The total water addition time was 45 minutes. The reaction mixture contains product, hydrochloric acid and unreacted acetophenone. The HCl was trapped in a caustic scrubber. The acetophenone removal is done by driving under high vacuum at temperature below  $100^\circ\text{C}$ . The PVP crystals were filtered and washed with HCl 37%.

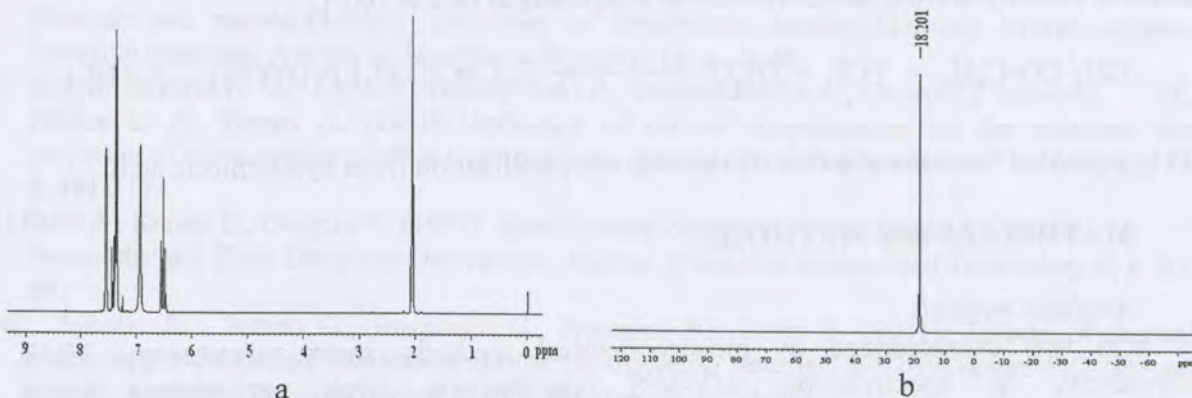
**RESULTS**

The PVP acid was characterized by mass spectroscopy (MS), NMR spectroscopy, IR spectroscopy, UV-VIS spectroscopy, high performance liquid chromatography (HPLC) and thermogravimetric analysis (TG).

The MS spectra was recorded with an Bruker Daltonik Esquire 6000, equipped with ESI (Electrospray ionization). From MS spectra was noticed that the molecular pick was found at  $m/z=182$ .

The HPLC system used in this work was a Jasco PU-1580 solvent delivery system and a MD-1510 UV/VIS detector, with a  $10\ \mu\text{l}$  flow cell. A reversed-phase Nucleosil C18 column ( $25\ \text{cm} \times 4\ \text{mm}$ ,  $\mu\text{particle size}$ ) was used for separation. A Reodyne 7725 injector with a  $10\ \mu\text{l}$  external loop was used for sample introduction. A Borwin Chromatography workstation was used to control the operation of HPLC, obtain the chromatogram, and perform data calculation. In HPLC appear a single signal, this proves that the analyzed sample contains a single compound with  $t_r=3.180\ \text{min}$ .

The  $^1\text{H}$ ,  $^{31}\text{P}$  NMR spectra were recorded with a Bruker DRX 400 MHz spectrometer in  $\text{CDCl}_3$ . In Figure 1 is shown the 1D-NMR spectra.



**Figure 1.**  $^1\text{H}$ -NMR (a) and  $^{31}\text{P}$ -NMR (b) spectra of PVP

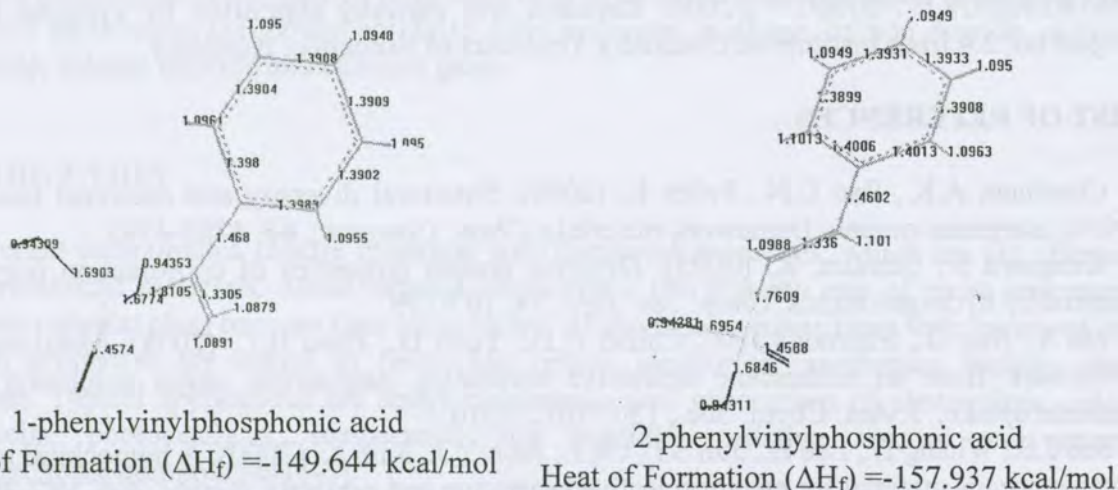
From NMR spectra the following data were collected: <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>): δ: 2.15 (s, P-OH) 6,51 (t, <sup>3</sup>J<sub>HH</sub> = 12,3 Hz, <sup>3</sup>J<sub>HP</sub> = 29,8Hz, =CH), 6.70-7.90 (m, C<sub>6</sub>H<sub>5</sub>-); <sup>31</sup>P-RMN (162MHz, CDCl<sub>3</sub>):δ: 18.20 ppm, s.

From UV-VIS spectra recorded in methanol with a CECIL CE 720 result a maximum absorbtion at λ=240 nm due to π-π\* interactions.

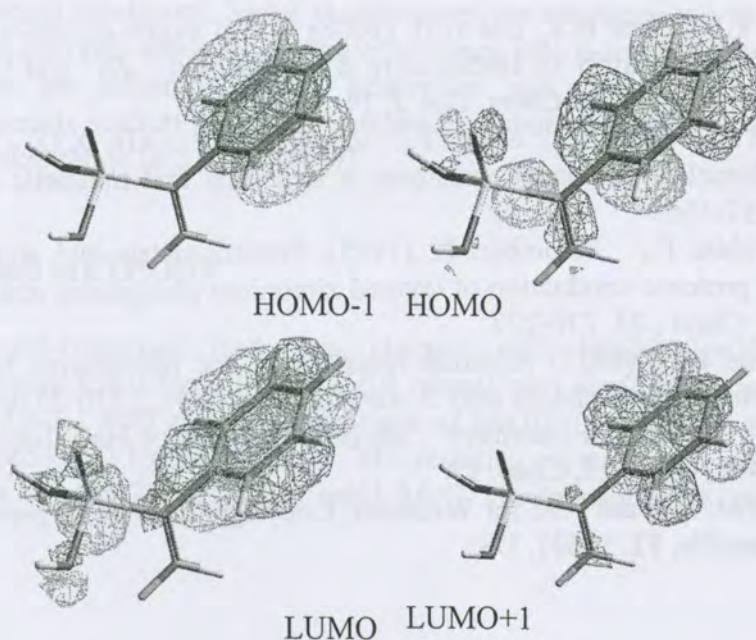
The infra-red spectrum of PVP recorded as a KBr pellet with Jasco-FT/IR-4200, contains a broad band at 2500-3700 cm<sup>-1</sup> corresponding to P-OH group, at 1698 cm<sup>-1</sup> corresponding to C=C group, at 1202 cm<sup>-1</sup> appear the bands corresponding to aromatic moiety. The spectrum also contains two intense bands at 1070 and 964 cm<sup>-1</sup> correspond to -PO<sub>3</sub> stretching modes and two weaker bands at 777 and 702 cm<sup>-1</sup> belonging to the monosubstituted vinyl moiety.

A thermal gravimetric analysis was also performed on crystals of PVP and indicated a weight loss around 100°C corresponding to water traces and to the melting of PVP acid. At 520.2 °C which correspond to loss of the vinyl portion of the phosphonate, respectively.

The bond lengths and the heat of formations energies are presented in Figure 2 and the HOMO-LUMO orbitals are presented in Figure 3.



**Figure 2.** Bond lengths and heat of formations for phenylvinylphosphonic acid



**Figure 3.** The HOMO,LUMO orbitals of PVP**CONCLUSIONS**

- From the reaction of acetophenone, phosphorus trichloride and distilled water was obtained 1-phenylvinylphosphonic acid.
- The obtained compound was completely analyzed by mass spectroscopy, NMR, IR spectroscopy, UV-VIS spectroscopy, high performance liquid chromatography and thermogravimetric analysis.
- By PM3 semi-empirical calculations were extracted informations regarding the design, structural properties, thermodynamic and electronic properties.

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