



## An Efficient, New, Simple and Rapid Method for Synthesis and Isomerization of Heteropolyanion B-[PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup>

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In this article, microwave assisted synthesis of B-PW<sub>9</sub>O<sub>34</sub><sup>9-</sup> is investigated. This new method is an efficient, simple and green procedure for synthesis and isomerization of B-PW<sub>9</sub>O<sub>34</sub><sup>9-</sup> heteropolyanion under microwave irradiation. The reaction carried out using the microwave method possessed shorter reaction times and higher yields than the thermal method. The product was characterized by IR, XRD and cyclic voltammetric spectroscopy and compared with references. It has been established that the B-PW<sub>9</sub> isomer is formed from the deformation of A-PW<sub>9</sub> by a thermal process. This anion (B-PW<sub>9</sub>) is unstable in aqueous solution and converts to the thermodynamically more stable A-PW<sub>9</sub>, unless it is reacted with a transition metal cation. There are large numbers of equilibria among several different species in the solutions of polyoxometalates.

**Key Words:** Phosphotungstate, Heteropolytungstate, Microwave, Isomerization.

### INTRODUCTION

Heteropolyoxometalates are a large family of potent medicines due to their excellent antiviral and antitumor activity<sup>1-4</sup>, while their application in clinic meets great difficulties for their toxicity<sup>5</sup>. How to synthesize heteropolyoxometalate possessing high activity and low toxicity has become the focus in heteropolyoxometalate research. Previously reported polyoxometalates showing medicinal activities are all salts simple Na<sup>+</sup>, K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> etc. inorganic cations, in which only polyanion creates activity against virus<sup>6-8</sup>. In recent years the possible uses of polyoxometalate chemistry for sequestration and immobilization of nuclear wastes have been reinvestigated. The wide range of applications is mainly based on (i) the ability of polyoxometalates to act as electron and proton reservoirs and (ii) the extreme variability of their molecular properties including shape, size, acidity and charge<sup>9</sup>. The Keggin-type heteropolyacids are believed to have extensive prospects of application in synthesis chemistry since their acidity strength is higher than that of both mineral and Lewis acids. Moreover, they are easy to handle, non-volatile and non-explosive. The chemistry of A-PW<sub>9</sub> and B-PW<sub>9</sub> isomers has been investigated<sup>10-13</sup>. It has been established that the B-PW<sub>9</sub> isomer is formed from the deformation of A-PW<sub>9</sub> by a thermal process. This anion (B-PW<sub>9</sub>) is unstable in aqueous solution and converts to the thermodynamically more stable A-PW<sub>9</sub>, unless it is reacted with a transition metal cation. There are large

numbers of equilibria among several different species in the solutions of polyoxometalates. However, Finke and Droege<sup>14</sup> reported the synthesis of the same anion by the reaction of the lacunary trivacant B-PW<sub>9</sub>O<sub>34</sub><sup>9-</sup> anion with Co<sup>2+</sup> ions, obtaining better yields and without any by-products. Also, our group synthesized new sandwich-type cadmium-containing heteropolytungstate by this anion<sup>15</sup>. In continuation of our group research on the syntheses and application of heteropolyacids in organic syntheses<sup>16-22</sup>, we hereby report the new and rapid method in synthesis and isomerization of B-PW<sub>9</sub>O<sub>34</sub><sup>9-</sup> heteropolyanion under microwave irradiation. We wish report an efficient and simple method for synthesis of this heteropolyanion.

### EXPERIMENTAL

Reagents and solvents used in this work are available commercially and used as received, unless otherwise indicated. All chemicals were purchased from Merck and used without purification. A LG-804 microwave was used for all experiments. <sup>1</sup>H NMR spectra were recorded on an FT-NMR Bruker 100 MHz aspect 3000. IR spectra were recorded on a Buck 500 scientific spectrometer (KBr pellets).

**Preparation of A-PW<sub>9</sub>:** Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (30 g, 0.09 mol) was dissolved in 37 mL of distilled water in a 250 mL beaker with a magnetic stirring bar until the solid is completely dissolved. Then 0.75 mL of (85 %) H<sub>3</sub>PO<sub>4</sub> was added dropwise

with stirring. After addition of the acid, the measured pH is 8.9 to 9.0. Glacial acetic acid (5.5 mL, 0.10 mol) is added dropwise with vigorous stirring. Large quantities of white precipitate form during the addition. The final pH of the solution is  $7.5 \pm 0.3$ . The solution is stirred for 1 h and the precipitate is collected and dried by suction filtration on a medium frit. 35 mL of HCl (12 M) is an alternative to acetic acid as the condensing acid; stirring is extended to 4 h before product collection. The crude product is suggested to be predominantly A- $\beta$ -Na<sub>8</sub>HPW<sub>9</sub>O<sub>34</sub>·24H<sub>2</sub>O (abbreviated as A-PW<sub>9</sub>).

#### General procedure for the preparation of B-PW<sub>9</sub>

**Method I (conventional heating):** After heating of A- $\beta$ -Na<sub>8</sub>HPW<sub>9</sub>O<sub>34</sub> (A-PW<sub>9</sub>) at 120 °C a solid state isomerization was induced and B- $\alpha$ -Na<sub>8</sub>HPW<sub>9</sub>O<sub>34</sub> (B-PW<sub>9</sub>) formed. This isomer is characterized by a marked change in the IR phosphate stretching region (1200-1020 cm<sup>-1</sup>). The extent of isomerization is somewhat erratic.

**Method II (microwave irradiation):** In order to prepare the B-PW<sub>9</sub> isomer from the deformation of A-PW<sub>9</sub>, it was exposed to microwave irradiations in 40 min. pulses each at 1000 W. For this purpose we first carried out the reaction in the presence of the A-PW<sub>9</sub> under microwave irradiation in 10 min. pulses each at 1000 W. and keep it on 4 times. The B- $\alpha$ -Na<sub>8</sub>HPW<sub>9</sub>O<sub>34</sub> (B-PW<sub>9</sub>) was characterized by IR spectroscopy.

### RESULTS AND DISCUSSION

Present results convincingly demonstrate that the use of this microwave oven technique can lead to substantial savings in time for many laboratory syntheses. This method provides rapid and relatively inexpensive access to very high temperatures and pressures. In the conventional method we need to heat at about 120 °C for isomerization of A- $\beta$ -Na<sub>8</sub>HPW<sub>9</sub>O<sub>34</sub> form to B- $\alpha$ -Na<sub>8</sub>HPW<sub>9</sub>O<sub>34</sub>. Several groups have reported conventional preparation methods which require several hours<sup>23</sup>. In our method, isomerization was not efficient at 100-300 W even by prolonging the reaction time. The range of 300-500 W afforded the product in low to moderate yields. Performing the reaction at 700-800 W gave good yields in relatively long reaction times. The best results were obtained at 1000 W (Table-1). Thus, all reactions were carried out at this power.

When A-PW<sub>9</sub> was irradiated in microwave oven at 1000 W for 40 min, the product was characterized by IR (Fig. 1) and cyclic voltammogram (Fig. 2) spectroscopy (Fig. 3). This summarization is characterized by a marked change in the IR phosphate stretching region (1200-1020 cm<sup>-1</sup>).

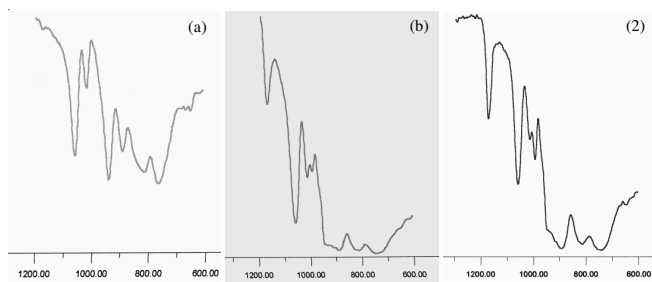


Fig. 1. IR spectrum of the deformation of A-PW<sub>9</sub> under microwave irradiation after (a) 20 min. (b) 30 min. (c) 40 min

Entry	MW power (W)	Time (min)	Yield <sup>a</sup> (%)
1	100	5 <sup>b</sup> (10)	4
2	200	5(10)	9
3	300	4(10)	13
4	400	4(10)	19
5	500	5(10)	37
6	600	5(10)	46
7	700	5(10)	52
8	800	4(10)	63
9	900	4(10)	67
10	1000	3(10)	74
11	1000	4(10)	76
12	1000	5(10)	71
13	1000	6(10)	70

<sup>a</sup> Isolated yield on the basis of the weight of the pure product obtained.  
<sup>b</sup> The reaction was carried out at 100 watts for 10 min. and continue 5 times.

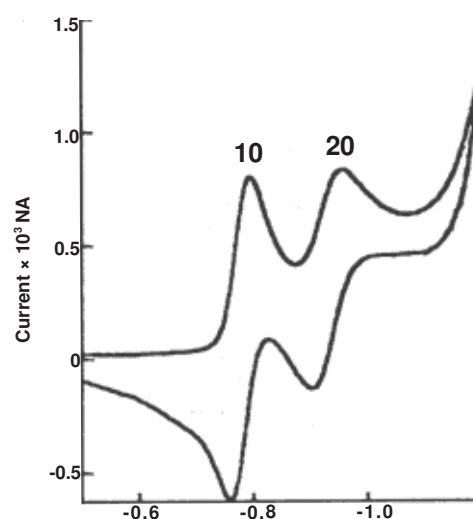


Fig. 2. Change of cyclic voltammetric feature of the deformation of A-PW<sub>9</sub> under microwave irradiation for 40 min

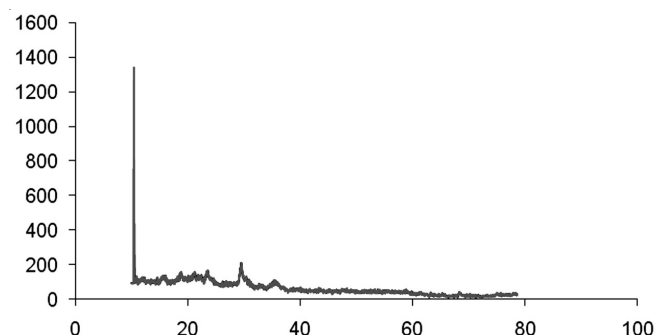


Fig. 3. Change of X-ray diffraction of the deformation of A-PW<sub>9</sub> under microwave irradiation for 25 min

Fig. 3. shows the XRD patterns for the deformation of A-PW<sub>9</sub> under microwave irradiation after 25 min. The typical reflexion at  $2\theta = 9^\circ$  is a typical feature of the Keggin structure<sup>24-26</sup>. The crystallinity of the POM prepared under thermal of microwave irradiation conditions is higher compared to the original procedure from Kozhevnikov<sup>27</sup>.

## Conclusion

A highly efficient, new, simple and rapid method in synthesis of B-PW<sub>9</sub>O<sub>34</sub><sup>9-</sup> heteropolyanion under microwave irradiation is successfully developed. Comparison between conventional heating and microwave irradiation revealed a specific and strong microwaves effect since, under conventional heating the reaction occurred in a very limited extension.

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