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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Microwave Synthesis of Vinylphosphonic Acid and Its Derivatives

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Abstract—Microwave Pyrolysis of β-substituted ethylphosphonic acid derivatives was studied. The resulting mixture of vinylphosphonic acid derivatives is similar to that obtained by convective heating.

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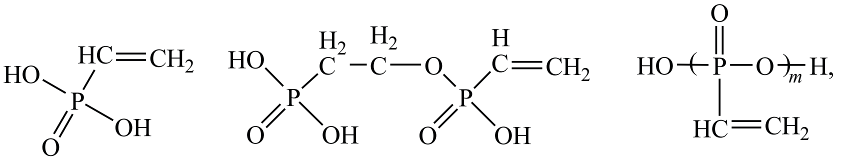
Vinylphosphonic acid and its derivatives have recently attracted researchers' attention, because conditions were found for preparing essentially new solid flame retardant homo- and copolymers of high molecular weight, 10^5–10^6 [1], exceeding by 2–3 orders of magnitude the molecular weight of the previously known products [2]. The most technologically convenient methods for preparing vinylphosphonic acid and its derivatives are based on pyrolysis of such derivatives as β-substituted (mainly β-acetoxy- or β-chloro-substituted) ethylphosphonic acid derivatives [3–8]. The pyrolysis is performed at 170–550°C (mainly at 190–270°C) in the presence of acid or base catalysts. The process occurs within 5–40 h and is accompanied by distillation of low-boiling products, with the mixture of vinylphosphonic acid derivatives remaining in the bottoms. The product composition depends on the reaction conditions. Pyrolysis of 2-chloroethylphosphonic acid or its aqueous solution yields a mixture of products containing, along with the unchanged starting compounds, also the compounds presented below, including vinylphosphonic acid polyanhydride [6]:



where m = 1–20.

The total content of vinylphosphonic acid and its derivatives reaches 73%. The distilled-off low-boiling fraction consists of water and hydrogen chloride.

The pyrolysis of technical-grade 2-chloroethylphosphonic acid and of samples of plant growth regulating agents, Kamposan M (30% aqueous solution of 2-chloroethylphosphonic acid) and 2-CEPA (50% aqueous solution of 2-chloroethylphosphonic acid), at 220–230°C and atmospheric pressure without catalyst for 10–15 h yields as bottoms the above-shown product mixture of approximately the same composition, with relatively complete release of hydrogen chloride and water [9–11]. The pyrolysis of dimethyl β-acetoxyethylphosphonate occurs with higher yield than that of β-chloroethylphosphonic acid, its aqueous solutions, and bis(β-chloroethyl) β-chloroethylphosphonate, but even in the presence of a catalyst the minimal time of pyrolysis of dimethyl β-acetoxyethylphosphonate is 5.5 h [3], and without catalyst it is 10–14 h [11]. Other β-substituted ethylphosphonic acid derivatives require considerably longer time to obtain similar yield of vinylphosphonic acid derivatives: 12–40 h and more [3–11]. Thus, the most significant drawback of the existing pyrolysis methods is long process time.

Microwave irradiation is one of the most promising ways to intensify the reactions. The major advantage of using microwave irradiation energy is considerably shorter reaction time, compared to the reactions performed under the conditions of traditional convective heating [12–15]. This also concerns organophosphorus synthesis [16].

This study deals with pyrolysis of β-substituted ethylphosphonic acids and their derivatives under the conditions of microwave irradiation. Our goal was to make shorter the time of synthesis of vinylphosphonic acid derivatives, to compare the composition of the products with that of thermal pyrolysis products, and to examine the possibility of using the products obtained for the production of phosphorus-containing fire retardants and ion-exchange materials. The products obtained by thermal and microwave pyrolysis were studied by ^{1}H and ^{31}P NMR spectroscopy and by elemental analysis, and their bromine and acid numbers were determined. Pyrolysis was performed by a standard procedure without catalyst. The starting compounds were bis(β-chloroethyl) β-chloroethylphosphonate (**1**), dimethyl β-acetoxyethylphosphonate (**2**), technical-grade β-chloroethylphosphonic acid (**3**), and commercial Kamposan (**3a**) and 2-CEPA (**3b**). In all the cases, the process was complete within 4–12 min. A distillate of low-boiling products and a bottom residue were obtained. The bottom residue was a mixture of vinylphosphonic acid derivatives of approximately the same composition as in thermal pyrolysis of the same substance. The composition of the distillate of low-boiling products was determined by elemental analysis and from physicochemical constants after the repeated fractionation, and also by gas chromatography–mass spectrometry. It was also essentially similar to the composition of the distillate obtained by thermal pyrolysis. The results of pyrolysis of β-chloroethylphosphonic acid and β-substituted ethylphosphonates under microwave irradiation are given in the table.

The data proving the structures of the products obtained and the compositions of the distillate and bottoms in microwave pyrolysis of bis(β-chloroethyl) β-chloroethylphosphonate (**1**) were reported previously [9]. Microwave pyrolysis of a melt of technical-grade β-chloroethylphosphonic acid or of its aqueous solutions yields bottoms containing a mixture of products similar in composition to products of common thermal pyrolysis. Along with vinylphosphonic acid and its polyanhydrides with various degrees of condensation, it contained the unchanged β-chloroethylphosphonic acid (up to 5–7%) and product of its condensation with one of acid groups of vinylphosphonic acid (β-phosphorylethyl hydrogen vinylphosphonate).

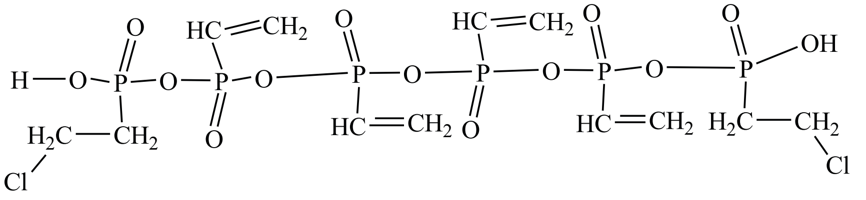
In the ^{1}H NMR spectrum of the product, there are signals from vinyl protons at 6.01, 6.15, and 6.25 ppm. The signal from the methylene group directly bonded to the P atom considerably decreases in intensity. The presence of the vinyl group is confirmed by the presence in the ^{1}H NMR spectrum of a typical ABX pattern due to diastereotopism of H_A, H_B, and H_X protons with the corresponding coupling constants J_{AB} = 2.2, J_{AX} = 17.9, and J_{BX} = 12.0 Hz. In addition, in the ^{1}H NMR spectrum

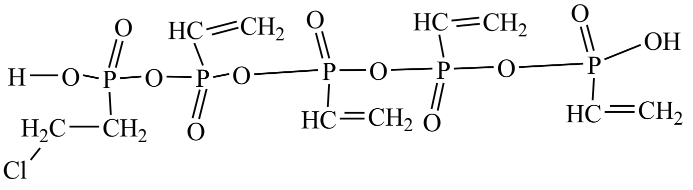
Microwave pyrolysis of β-chloroethylphosphonic acid and its derivatives (220–230°C, air, atmospheric pressure, no catalyst)

Starting compd.	Composition of bottom residue, %					Composition of low-boiling fractions, %						Reaction time, min
	dialkyl vinyl-phos-phonate	monoalkyl hydrogen vinyl-phos-phonate	vinyl-phos-phonic acid	pyro derive-atives of vinyl-phos-phonates	total vi-nyl-phos-phonate deriva-tives	methyl acetate	methanol	dimethyl ether	HCl	water	other prod-ucts	
1	–	54.0	14.6	21.4	90	–	–	–	4	1	95	5–12
2	10	31	10	43	94	95	2	2	–	1	–	4–10
3	–	–	11	66	77	–	–	–	97	–	3	5–10
3a, 3b	–	–	10	63	73	–	–	–	50–30	50–70	–	6–10

the triplet of chloromethyl protons (3.65 ppm, $J = 5.1$ Hz) considerably decreases in intensity. The ^{31}P NMR spectrum of the products confirms the presence of vinylphosphonic acid: A well-defined signal is observed at 22 ppm. Potentiometric titration with alkali revealed two jumps corresponding to neutralization of acid groups of various strengths. The shape of the potentiometric titration curve suggests the presence of a compound containing dibasic acid fragments. The presence of acid OH groups is also confirmed by the ^{1}H NMR spectrum (11.55 and 11.96 ppm).

The results of elemental analysis for chlorine (~6–8%) and phosphorus (~21–30%) and comparison of the bromine number found with the theoretical value suggest that the pyrolysis products can contain, along with the above-mentioned compounds, also the following polyanhydride structures:





In the distillate, within 4–10 min we obtained an aqueous HCl solution in an amount close to the expected level. Elimination of HCl with the formation of vinyl groups was confirmed by the results of double bond determination in the bottoms (bromide–bromate method) and by ^{1}H and ^{31}P NMR spectroscopy.

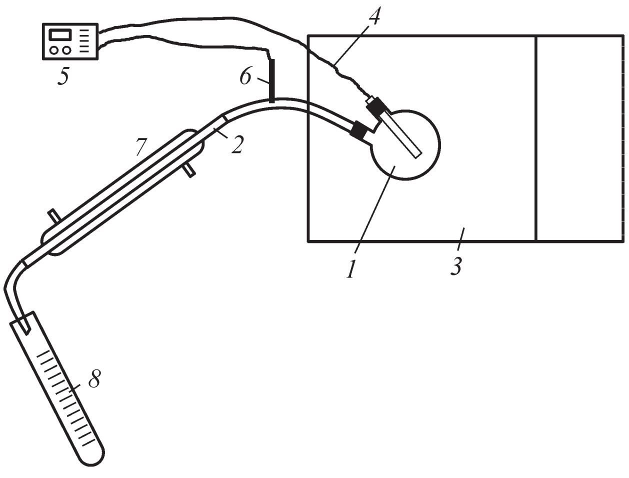
It should be particularly noted that the total yield of vinylphosphonates and their derivatives in the microwave synthesis was in all the cases somewhat higher than in thermal pyrolysis, although we did not examine the influence of the process temperature on the yield of the mixture of vinylphosphonic acid derivatives for each starting compound used. The temperature conditions of the synthesis were chosen by analogy with those used most frequently in thermal pyrolysis [3–11]. It should also be noted that considerable shortening of the process time in microwave irradiation could also result in decreased amount of tars, with a simultaneous increase in the content of pyrovinylphopshonic acid derivatives. An increase in the raw material amount loaded (from 10 to 100 g) is accompanied by an increase in the microwave synthesis time from 4–5 to 10–12 min, but in all the cases the time required to obtain approximately equal amounts of a mixture of target products under microwave irradiation is by two and more orders of magnitude shorter than in common pyrolysis

By now, there is no common concept of the mechanism of reaction acceleration under the action of microwave radiation. Rakhmankulov et al. [14] believe that acceleration of chemical reactions is due to more intense heat supply to the reaction zone. Based on analysis of numerous studies, There are substantiations concerning both the occurrence of microwave catalysis and the possibility of alternative reaction mechanisms [12]. In view of the fact that, in this study, experiments were performed with small amounts of substances (5–100 g), it is hardly convincing to attribute considerably lower reaction rate at thermal heating to slow heating of the reactants, because heating with vigorous stirring on a silicone oil bath at 230–250°C is very fast. We believe that acceleration of chemical transformations in our process may be due to the microwave effect, making the time required for the reaction completion shorter by two orders of magnitude.

EXPERIMENTAL

For the pyrolysis, we used samples of technical-grade 2-chloroethylphosphonic acid, technical-grade bis(β-chloroethyl) β-chloroethylphosphonate, and commercial 2-CEPA produced by the Khimprom Volgograd Research Center with the parameters meeting the requirements of semicommercial production regulations, and also a sample of Kamposan M produced by Bitterfeld Chemical Combine (Germany). The starting dimethyl hydrogen phosphite [TU (Technical Specifications) 6.36.576344-6–88] was vacuum-distilled with collection of the fraction boiling at 56–58°C (10 mm Hg), n_D^{20} 1.4035. Dimethyl β-acetoxyethylphosphonate was synthesized as described in [17]. We obtained the product with bp 116–118°C (2 mm Hg), n_D^{20} 1.4321 {published data: bp 182–194°C (5–6 mm Hg), n_D^{20} 1.4369 [17]; 95–97°C (0.15 mm Hg), n_D^{20} 1.4316 [18]}. The IR spectra were recorded with a Specord M82 spectrometer, and the ^{1}H NMR spectra, with a Varian Mercury-300 spectrometer operating at 300 MHz, internal reference HMDS, solvent DMSO; the ^{31}P NMR spectra were recorded with a Varian Mercury-300 spectrometer operating at 121.4 MHz, relative to 85% H_3PO_4. The mass spectra were taken with a Varian MAT-111 gas chromatograph–mass spectrometer at the ionizing electron energy of 70 eV.

Standard procedure of microwave synthesis. A weighed two-necked reactor (see figure) was charged with a sample of the starting organophosphorus compound. Reactor *1* was attached to Teflon fitting *2* inserted through the wall of an Elektronika SP01 microwave oven *3* with M-105-I magnetron (2400 MHz, 630 W). A KIKhA 02.01-C321-I-3-160/3500 thermocouple *4* in glass cladding was inserted through the second neck. The pyrolysis temperature was controlled with a PID control unit Metakon-523 *5*. The pyrolysis temperature was constant in all the experiments, 220–230°C. Within a few minutes after switching on the microwave oven, we observed evolution of vapors of low-boiling products (temperature growth was monitored with a TP-0198/1 KhA thermocouple *6*), which condensed in a descending water-cooled Liebig condenser *7*. The condensate was collected in a weighed volumetric test tube *8* and analyzed. After the distillation completion, the oven was switched off and the bottoms were cooled, weighed, and analyzed.



Scheme of laboratory installation for microwave synthesis: (*1*) reactor, (*2*) fluoroplastic tube, (*3*) microwave oven, (*4, 6*) thermocouples, (*5*) PID controller, (*7*) Liebig condenser, and (*8*) receiver.

CONCLUSIONS

(1) Microwave irradiation at 220–230°C without catalyst, compared to convective heating, allows synthesis of vinylphosphonic acid derivatives with the same product composition but in somewhat higher yield within 4–12 min instead of 12–40 h required in the case of convective heating.

(2) The pyrolysis acceleration is attributed to the microwave effect.

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