ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 7, pp. 1055–1058. © Pleiades Publishing, Inc., 2006.
Original Russian Text © S.N. Bondarenko, T.V. Khohlova, S.A. Orlova, O.I. Tuzhikov, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 7, pp. 1102–1106.

Synthesis of Oligomeric Boron-containing Phosphopolyols

S. N. Bondarenko[a], T. V. Khohlova[b], S. A. Orlova[b], and O. I. Tuzhikov[b]

[a] *Volzhskii Polytechnical Institute, Volgograd, Russia*
[b] *Volgograd State Technical University, pr. Lenina 28, Volgograd, 400131 Russia*

Received July 6, 2005

Abstract — Transesterification of phosphorus-containing esters of boric acid with glycols leads to formation of polyols, the promising antipyrenes. Structure and reactivity of the oligomeric boron-containing polyols are studied.

DOI: 10.1134/S1070363206070085

The boric acid polyesters reveal undoubtful interest in the synthesis of organoboron compounds [1, 2]. The polyesters form a synthetically available and inexpensive class of organoboron compounds characterized by high thermostability, usually stable to oxidation, exhibit high adhesion to materials of various nature, and are widely used as the components in various compositions. Some representatives of these polymers may be used for manufacturing films and fibers [3].

Investigations in the field of organoboron polymer synthesis have shown [4] that the products of reaction of 1,2-, 1,3-diols and aromatic *ortho*-diols with boric acid and boron chloride are acidic esters condensing at elevated temperature to dimers with a five-membered ring. With a diol excess the diborates containing B(III)–O–R fragment are formed. The 1,3-diols in the reaction with boric acid form the most stable non-strained rings bound with one another by methylene-diborate fragment [5]. Heating of boron triacetate with glycerol in a vacuum gives polymeric triol borates, the glass-like polymers. Tetraols are esterified with boric acid to form polyesters or boric acids [2]. Hence, investigation of the methods for obtaining the boric acid based compounds opens a wide perspective for development new directions in the organoboron synthesis.

It is known that dimethyl hydrogen phosphite derivatives were used for the synthesis of organophosphorus esters by transesterification with some glycols [6]. Investigation of structure of the products of trans-esterification has shown that in the case of ethylene glycol [7] the substances related to ten-membered cyclic bisphosphite are formed. The transesterification by diethyleneglycol and triethyleneglycol leads to formation of linear polyphosphates [8].

In the preceeding report we have presented results of investigation of the boric acid reaction with dimethyl hydrogen phosphite leading to oligomeric borates [9]. The aim of this work is the investigation of the oligomeric borate reaction with glycols, considering the reaction pathway, and study of structure and properties of the functional boron-containing phosphopolyols, the promising antipyrenes for the various polymers.

We found that the oligomeric borate can react with ethylene glycol, diethylene glycol, glycerol and 1,4-butanediol to form linear boron-containing phosphopolyols. Reaction was carried out under noncatalytic conditions either with stoichiometric amounts of reagents or with an excess of the glycol, without a solvent, at 170–200°C under an inert gas. The boron-containing phosphopolyols obtained are viscous liquids either colorless or of amber coloration. Their physicochemical characteristics are listed in Table 1.

The IR spectra of obtained compounds contain the bands characteristic of bond vibrations of the following groups. A strong band at 3330–3350 cm^{-1} relates to hydroxy groups. A band of middle intensity at 2460–2468 cm^{-1} is characteristic of PH bond. An absorption band at 1456–1458 cm^{-1} is attributed to B(III)–O group. The band at 1410–1450 cm^{-1} is characterstic of $–CH_2–$ group. Strong absorption bands at 1220–1230 cm^{-1} relate to P=O group, and at 1008 cm^{-1} to P–O–C fragment.

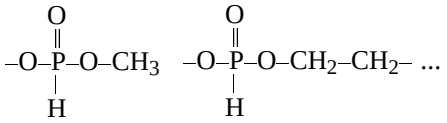
The ^1H NMR spectra of the oligomeric compounds almost not differ from one another, therefore we restricted ourselves to describing thoroughly only one of them. ^1H NMR spectrum of compound obtained by the reaction of oligomeric borate with ethylene glycol contains the signals of the phosphite group

Table 1. Physicochemical properties of oligomeric boron-containing phosphopolyols

Oligomeric borate : glycol, mol : mol	M	n_D^{20}	ν, St	ρ_4^{20}, g cm^{-3}	Found P, %	Calculated P, %
Ethylene glycol						
1:1	1520	1.4788	34.3	1.3184	29.4	30.6
1:2	820	1.4748	32.7	1.2573	18.8	20.0
Diethylene glycol						
1:1	1810	1.4784	31.8	1.9395	26.8	26.8
1:2	910	1.4730	30.1	1.8839	17.2	17.8
Glycerol						
1:1	1750	1.4876	35.2	1.5921	27.8	30.5
1:2	890	1.4842	33.8	1.4486	17.8	19.4
1,4-Butanediol						
1:1	1740	1.4827	33.5	1.7235	28.1	30.2
1:2	880	1.4797	31.3	1.6243	18.4	20.2

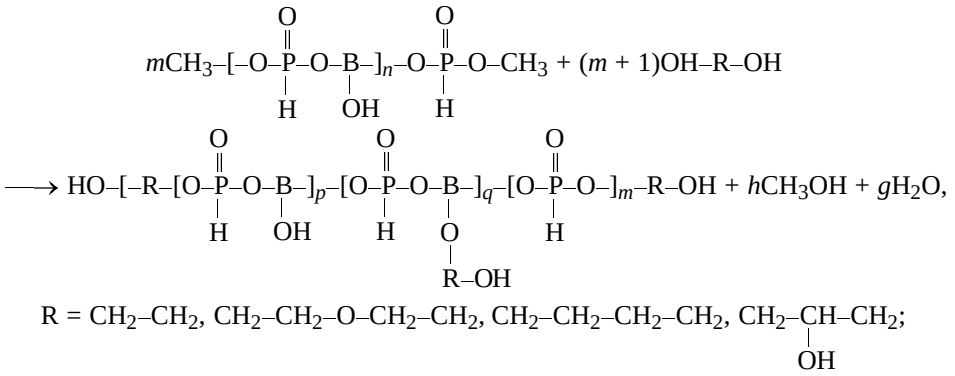
including a strong doublet at δ 7.05 ppm (J_{HP} 656 Hz) and a low intensity doublet at δ 6.9 ppm (J_{HP} 688 Hz). We suggest that this compound contains two types of the protons of phosphite group with different chemical surrounding, that is with methoxy substituent and without it. Intensity of the signal of the phosphite proton related to the group with methoxy substituent is very low. Obviously, the reaction proceeds with the methanol elimination by the methoxyphosphite groups, and this was confirmed experimentally. The ^{1}H NMR spectrum also contains complex signal at δ 4.70–4.22 ppm, evidently belonging to the protons of the side hydroxymethylene group of the oligomer. The multiplet signal at δ 3.90–3.75 ppm relates to the internal oxymethylene group protons. The signal at δ 3.61 ppm corresponds to the protons of methoxy group bound to phosphorus. The doublet that usually observed in such cases overlaps here with closely located multiplet of oxymethylene group and another half of the signal is not observed. The signal of the acidic group proton is located at δ 11.20 ppm.

Analysis of ^{31}P NMR spectra of the oligomeric borate and the products of its reaction with glycols shows that phosphite groups with different chemical surrounding are present in the structure of the reaction product. In the proton decoupled ^{31}P NMR spectrum of the product obtained by the reaction with ethylene glycol the phosphite groups are characterized by signals at δ_P 6.62, 5.52, and 3.63 ppm. In ^{31}P NMR spectrum without the proton decoupling these signals have the coupling constants J_{HP} 690, 689, and 770 Hz respectively. Hence, we can conclude on the different surrounding of phosphorus atom.



The phosphorus atom in oligomeric product structure obviously exists mainly as the phosphorous acid derivative. Amount of phosphorus-containing groups of another nature (possibly the phosphate one) is not more than 5 wt%.

Hence, reaction proceeds according to the following scheme:



n = 4–5, $p + q$ = 4–5, m = 1–2, $h = 2m$, $g = qm$.

Table 2. Activation and thermodynamic parameters of oligomeric borate polycondensation with glycols

Glycol	E_a, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} deg^{-1}	$\Delta G^{\neq}$, kJ mol^{-1}
Ethylene glycol	96.552	92.748	–94.305	135.934
Diethylene glycol	121.304	117.500	–35.517	133.762
Glycerol	122.687	108.883	–57.745	135.320
1,4-Butanediol	113.850	110.043	–47.611	131.843

For the estimation glycol reactivity in the reactions with oligomeric borates and elucidation the reaction activation parameters we carried out kinetic studies in the temperature range 170–200°C. The reaction kinetics was monitored by the measuring amount of the methanol evolved (Fig. 1).

The reaction order was evaluated by the graphical method. It was established that the reaction under investigation proceeds according to the second order kinetic equation. As the anamorphose in $\ln K_{av}$–$(1/T)$ coordinates is linear, the polycondensation activation parameters obey the Arrhenius equation (Fig. 2).

Parameters of the equations were calculated by the root-mean-square method. On their basis the activation energy and thermodynamic characteristics of the reaction were evaluated. Obtained values are listed in Table 2.

Considering the obtained reaction rate constants of methylphosphite borate polycondensation with glycols it is possible to establish the following reactivity series: ethylene glycol > 1,4-butanediol > diethylene glycol > glycerol.

EXPERIMENTAL

IR spectra of suspensions in vaseline oil were recorded on a Specord M-82 spectrometer. ^{1}H NMR spectra were taken on a Bruker AC-200 (200 MHz) spectrometer in DMF-d_6, ^{31}P NMR spectra were obtained on a Bruker AC-200 spectrometer (80 MHz) in DMF-d_6 against external 85% phosphoric acid with the accuracy 0.02 and 0.01 ppm respectively.

Kinetic experiments were carried out in thermostated reactor equipped with a jacket, a thermometer, a condenser, and a bubbler. Temperature was maintained with accuracy ±0.2°C. The process was carried out under an inert gas flow. Reaction progress was monitored by measuring the methanol evolution. Evolving water-methanol mixture was distilled off and weighted. Content of methanol was evaluated by a procedure including its oxidation with potassium permanganate in acidic medium to formaldehyde and colorimetric evaluation of the latter in the presence of chromotropic acid [10]. Besides, picnometric measuring of the water-methanol mixture density was carried out [11]. From the data obtained the kinetic curves for different concentrations and molar ratio of starting reagents were plotted. Investigations were carried out in the temperature range 170–200°C. Kinetic curves

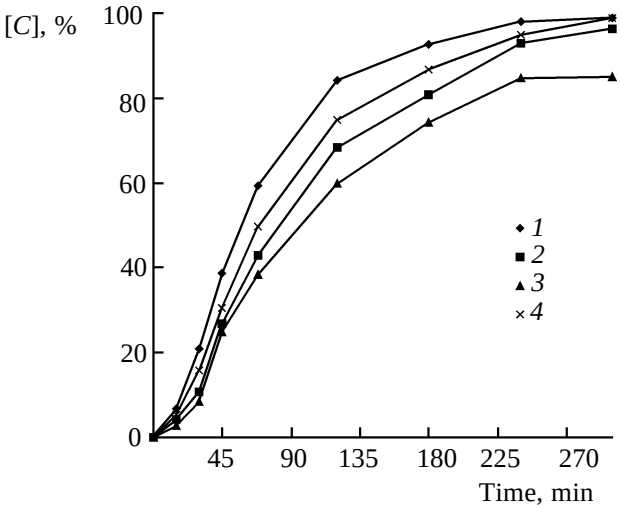


Fig. 1. Dependence of the evolved methanol amount on the reaction duration. Conditions of the reaction: *T* 180°C, oligomeric borate to glycol molar ratio 1 : 2; boron-containing phosphopolyols on the basis (*1*) ethylene glycol, (*2*) diethylene glycol, (*3*) glycerol, (*4*) 1,4-butanediol.

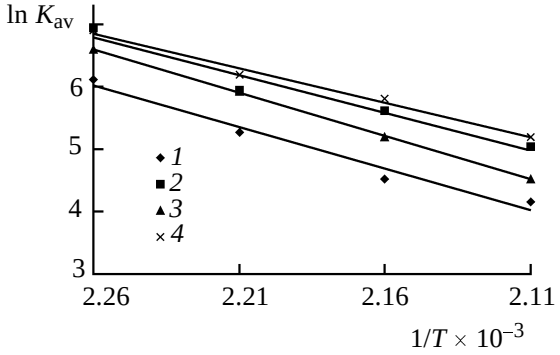


Fig. 2. Dependence of $\ln K_{av}$ on $1/T \times 10^{-3}$. Boron-containing phosphopolyols on the basis (*1*) ethylene glycol, (*2*) diethylene glycol, (*3*) glycerol, (*4*) 1,4-butanediol.

were analyzed by means of graphical differentiation. Reaction order, rate constants and their temperature dependence were evaluated. Results of kinetic studied were treated by the root-mean-square procedure [12].

Boron-containing phosphopolyol on the basis of ethylene glycol. Oligomeric borate, 20 g, and 3.10 g of ethylene glycol were mixed. Reaction was carried out under argon at 170-190°C for 5 h with distilling the water–alcohol fraction off. The reaction progress was monitored by weighting the evolved water–alcohol fraction. Its final quantity was 2.02 g. The methanol content in the liquid phase was 1.58 g. The obtained product was kept in a vacuum at 160–180°C. Yield of oligomeric boron-containing phosphopolyol was 21.07 g. Reaction product is a viscous colorless liquid well soluble in water, DMF, acetone, alcohols. The IR spectrum, ν, cm^{-1}: 3350, 2462, 1168, 1540, 1456, 1412, 1225, 1010. The ^1H NMR spectrum (DMF-d_6), δ, ppm: 11.20, 7.06, 6.90, 4.68, 4.47–4.23, 3.75, 3.61. The ^{31}P NMR spectrum (DMF-d_6), δ_P, ppm: 30.78, 24.68, 6.55, 5.52, 3.64. Found, %: C 13.1; H 3.8; P 18.8.

Boron-containing phosphopolyol on the basis of diethylene glycol. Oligomeric borate, 20 g, and 5.3 g of diethylene glycol were mixed. Reaction was carried out at 170–190°C under argon for 5 h with distilling the water-alcohol fraction off. The reaction progress was monitored by weighting the water–alcohol fraction evolved (total weight 1.96 g). The methanol content in the liquid phase was 1.54 g. The product obtained was kept in a vacuum at 160–180°C. Yield of the oligomeric boron-containing phosphopolyol was 23.30 g. Reaction product is viscous colorless liquid well soluble in water, DMF, acetone, alcohols. The IR spectrum, ν, cm^{-1}: 3348, 2460, 1660, 1540, 1456, 1432, 1228, 1008. The ^1H NMR spectrum (DMF-d_6), δ, ppm: 11.60, 7.55, 6.45, 4.68, 4.55–4.22, 3.83, 3.64. The ^{31}P NMR spectrum (DMF-d_6), δ_P, ppm: 30.89, 24.80, 6.61, 3.67. Found, %: C 21.8, H 5.4, P 17.2

Boron-containing phosphopolyol on the basis of glycerol. Oligomeric borate, 20 g, and 4.6 g of glycerol were mixed. The reaction was carried out under argon at 170-190°C for 5 h with distilling the water–alcohol fraction off (total weight 1.8 g). The methanol content in water phase was 1.36 g. The product obtained was kept in a vacuum at 160–180°C. Yield of oligomeric boron-containing phosphopolyol 22.8 g. The reaction product is a viscous amber-colored mass soluble in water and DMF. The IR spectrum, ν, cm^{-1}: 3346, 2428, 1636, 1520, 1456, 1424, 1230, 1008. The ^1H NMR spectrum (DMF-d_6), δ, ppm: 11.24, 7.1, 6.9, 4.48–4.28, 3.9–3.64, 4.60. The ^{31}P NMR spectrum (DMF-d_6), δ_P, ppm: 30.97, 24.67, 6.55, 3.64. Found, %: C 17.6, H 4.4, P 17.8.

Boron-containing phosphopolyol on the basis of 1,4-butanediol. Oligomeric borate, 20 g, and 1.4 g of 1.4-butanediol were mixed. Reaction was carried out under argon at 170–190°C for 5 h with distilling the water–alcohol fraction off (total weight 1.98 g). The methanol content in liquid phase 1.58 g. The product obtained was kept in a vacuum at 160–180°C. Yield of oligomeric boron-containing phosphopolyol 22.5 g. The obtained product is a viscous amber-colored mass, soluble in water and DMF. The IR spectrum, ν, cm^{-1}: 3342, 2464, 1636, 1528, 1456, 1438, 1220, 1008. The ^1H NMR spectrum (DMF-d_6), δ, ppm: 11.20, 7.10, 6.86, 4.48–4.28, 4.00–3.82, 3.64. The ^{31}P NMR spectrum (DMF-d_6), δ_P, ppm: 30.97, 24.67, 6.55, 3.63. Found, %: C 22.4, H 5.6, P 18.4.

REFERENCES

1. Jererd, W., *Khimiya organicheskikh soedinenii bora* (Chemistry of Organoboron Compounds), Zhigach, A.F., Ed., Moscow: Khimiya, 1966.
2. Korshak, V.V., Zamyatina, V.A., and Bekasova, N.I., *Boroorganicheskie polimery* (Organoboron Polymers), Moscow: Nauka, 1975.
3. Freiser, A.G., *Vysokotermostoikie polimery* (High Thermostability Polymers), Pravednikov, V.P., Ed., Moscow: Khimiya, 1971.
4. Musina, E.I., Nikonov, G.N., Balueva, A.S., and Litvinov, I.A., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 3, p. 422.
5. Musina, E.I., Litvinov, I.A., Balueva, A.S., and Nikonov, G.N., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 3, p. 429.
6. Tuzhikov, O.I., Dhaibe, M.Kh., and Khohlova, T.V., *Khimiya i tekhnologiya elementoorganicheskikh monomerov i polimernykh materialov* (Chemistry and Technology of Organoelement Monomers and Polymeric Materials), Volgograd: Mezhvuz. Sbornik Nauchnykh Trudov Volg.GTU., 1998, p. 108.
7. Petrov, K.A., Nifant'ev, E.V., and Goltsova, R.G., *Zh. Obshch. Khim.*, 1963, vol. 33, no. 2, p. 1485.
8. Petrov, K.A. and Gol'tsova, R.G., *Usp. Khim.*, 1966, vol. 35, no. 11, p. 1484.
9. Bondarenko, S.N., Khohlova, T.V., Orlova, S.A., Derbisher, V.E., Tuzhikov, O.I., and Dhaibe, M.Kh., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 9, p. 1460.
10. Novikov, Yu.V., Lastochkina, K.O., and Boldina, Z.N., *Metody issledovaniya kachestva vody vodoemov* (Methods of Investigation of Water Quality in Basins), Shipkova, S.A., Ed., Moscow: Meditsina, 1990.
11. Stepin, V.D., *Tekhnika laboratornogo eksperimenta v khimii* (Technique of Laboratory Experiment in Chemistry), Moscow: Khimiya, 1999.
12. Leydner, K., *Kinetika organicheskikh reaktsyi* (Kinetic of Organic Reactions: Moscow: Mir, 1966.