SYNTHESIS OF PHOSPHORUS-CONTAINING POLYESTERS BY THE REACTION OF HOMOPOLYTRANSESTERIFICATION

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Abstract

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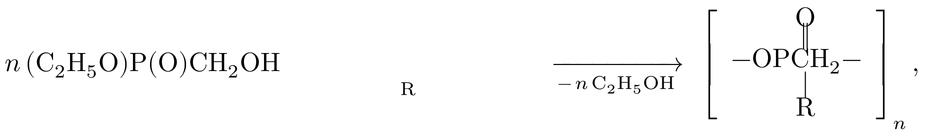
SYNTHESIS OF PHOSPHORUS-CONTAINING POLYESTERS BY THE REACTION OF HOMOPOLYTRANSESTERIFICATION

In previous communications (1, 2) we described the synthesis and properties of polyphosphites and polyphosphinites containing atoms of pentavalent or trivalent phosphorus in the main chain, obtained by the reaction of polytransesterification of complete esters of phosphonic and phosphinic acids with various glycols.

Continuing our investigations in the field of phosphorus-containing polyesters, we studied the reaction of homopolytransesterification of esters of oxymethylphosphinic acid. Reactions of this type have not been described in the literature.

As starting compounds for homopolytransesterification, we chose the ethyl ester of ethyl-(oxymethyl)-phosphinic acid and the ethyl ester of phenyl-(oxymethyl)-phosphinic acid, which have in the molecule two reactive functional groups. They were obtained by addition of the monoethyl ester of ethylphosphinous acid and the monoethyl ester of phenylphosphinous acid to formaldehyde in the presence of sodium ethylate, according to the procedure described for the preparation of the diethyl ester of oxymethylphosphonic acid (3). The use of molecular distillation of the reaction mixtures enabled us to obtain esters of oxymethylphosphinic acid in good yields (50–60%).

The homopolytransesterification reactions of esters of oxymethylphosphinic acids were carried out by heating them in the absence of catalysts:



$$n\,(C_2H_5O)P(O)CH_2OH \quad {}_{R} \xrightarrow[-n\,C_2H_5OH]{} \left[\,-O\overset{O}{\underset{R}{P}}CH_2-\,\right]_n,$$

where $R = OC_2H_5;\ C_2H_5;\ C_6H_5$.

Kinetic studies were carried out using the ethyl ester of ethyl-(oxymethyl)-phosphinic acid as an example. The rate of the homopolycondensation reaction was monitored by the amount of alcohol evolved. For rapid and complete removal of alcohol vapors through the reaction mixture during the reaction, a stream of dry nitrogen was passed at a constant rate.

The reactions were carried out at 180°, 200°, 220° (Fig. 1). With increasing temperature, the rate and degree of completion of the reaction (a) increase markedly. It was shown that the dependence of the values $(1-a)^{-1}$ on time (Fig. 2) up to 65% conversion is expressed by straight lines. This indicates that the reaction under study is a second-order reaction (4).

The rate constants of the polycondensation reaction of the ethyl ester of ethyl-(oxymethyl)-phosphinic acid at 180°, 200°, 220° have, respectively, the values $0.69 \cdot 10^{-4}$, $1.98 \cdot 10^{-4}$, $5.05 \cdot 10^{-4}$ mol/sec. The dependence of the logarithm of the reaction-rate constant on the reciprocal absolute temperature is expressed by a straight line, which is in accordance with the Arrhenius equation. The activation energy of this reaction is $23\,400 \pm 1000$ cal/mol.

Comparison of the results of studying the transesterification reaction of diethyl ethylphosphinate with ethylene glycol and the homopolycondensation of ethyl ethyl-(oxymethyl)-phosphinate shows that the rate of the latter, at the same temperatures, is somewhat higher at a lower activation-energy value.

As a result of the homopolytransesterification reaction of ethyl ethyl-(oxymethyl)-phosphinate, viscous liquids are obtained, ranging from colorless to pale-yellow, with molecular weight 700–800 (degree of polymerization 6–7). Upon further heating in vacuum, very thick, almost nonflowing polyesters with MW up to 2000 are formed. The polymers are soluble in dimethylformamide, alcohols, dioxane, and partly in benzene, and are insoluble in ether.

Fig. 1 and Fig. 2: kinetic plots

Fig. 1. Degree of completion of the reaction (a) in the homopolytransesterification of ethyl ethyl-(oxymethyl)-phosphinate:
1–180°, 2–200°, 3–220°

Fig. 2. Dependence of $(1-a)^{-1}$ on time in the homopolytransesterification reaction of ethyl ethyl-(oxymethyl)-phosphinate

It is interesting to note that, on standing for several hours at room temperature, a crystalline substance separates from the polyester obtained by homopolycondensation of ethyl ethyl-(oxymethyl)-phosphinate, in an amount up to 7% of the total weight of the polyester. The crystalline product is separated by filtration from dioxane solutions of the polyester. It is formed by intermolecular cyclization of the starting ester and is 1,4-dioxa-2,5-dioxido-2,5-diethyl-2,5-diphosphorinane:

$C_6H_{14}O_4P_2$

cyclic structure of 1,4-dioxa-2,5-dioxido-2,5-diethyl-2,5-diphosphorinane

$C_6H_{14}O_4P_2$. M.p. 210–212°; mol. wt. found 210; calculated 212.

Found, %: P 29.25; calculated, %: P 28.95

Analysis for the content of ethoxy groups gave a negative result. Evidence for the possibility of formation of similar products is available in the literature (5).

When this product was heated at a temperature above 220° for 5 h, a viscous polymer with mol. wt. 600 was obtained.

As is seen from Fig. 3, homopolycondensation of diethyl oxymethylphosphinate, which has three functional groups in the molecule,

groups (curve 2), proceeds faster than in the case of the monoethyl ester of ethyl- and phenyl-(oxymethyl)-phosphinic acid. In the first case, initially viscous polymers are formed, and upon further heating in vacuum, almost solid polymers. They apparently have a partially or completely cross-linked structure, since they do not dissolve in most organic solvents. When the reaction was carried out above 200°, partial resinification of the product was observed.

The rate of polycondensation of the ethyl ester of phenyl-(oxymethyl)-phosphinic acid at the first stage of the reaction differs little from the rate of polycondensation of the ethyl ester of ethyl-(oxymethyl)-phosphinic acid. Further study of the kinetics of homopolycondensation of the ethyl ester of phenyl-(oxymethyl)-phosphinic acid was not carried out because of the rapid increase in the viscosity of the reaction mass during the reaction (3–4 hours after the start of the reaction) and the associated difficulty in removing alcohol vapors. Upon further heating to 220–250° in vacuum at a residual pressure of 1 mm Hg, a solid, brittle, transparent polymer with a molecular weight of about 5000 is formed, soluble in dioxane and benzene, soluble in alcohol, and insoluble in ether.

Fig. 3. Degree of completion of the reaction (a) of homopolytransesterification of the ethyl ester of ethyl-(oxymethyl)-phosphinic acid (1), the diethyl ester of oxymethyldiphosphinic acid (2), and the ethyl ester of phenyl-(oxymethyl)-phosphinic acid (3)

Fig. 3. Degree of completion of the reaction (*a*) of homopolytransesterification of the ethyl ester of ethyl-(oxymethyl)-phosphinic acid (1), the diethyl ester of oxymethyldiphosphinic acid (2), and the ethyl ester of phenyl-(oxymethyl)-phosphinic acid (3)

To obtain the described polyesters it is also possible to use directly the reaction mixtures obtained as a result of addition of incomplete esters of phosphinous acids to formaldehyde, without preliminary isolation from them in pure form of the esters of oxymethylphosphinic acids. For this purpose the reaction mixtures were heated in vacuum at a residual pressure of 1-15 mm Hg and with a gradual increase in temperature to 250° for 5-7 hours.

Experimental Part

Ethyl ester of ethyl-(oxymethyl)-phosphinic acid. To 78.5 g of the monoethyl ester of ethylphosphinous acid and 19.3 g of polyoxymethylene were added several drops of an alcoholic solution of sodium ethylate. The reaction mixture was heated to 120°, after which the reaction proceeded spontaneously with evolution of heat, until complete dissolution of the polyoxymethylene. The alcoholate was neutralized with glacial acetic acid. The pure product was obtained after two distillations (yield 58%). B.p. 108-110°/ $2 \cdot 10^{-2}$ mm, n_D^{20} 1.4532, d_4^{20} 1.1202. Mol. wt. found 36.70; calculated 36.56.

Found, %: P 20.39. Calculated, %: P 20.10

Ethyl ester of phenyl-(oxymethyl)-phosphinic acid. The reaction was carried out analogously. The pure product was obtained after preliminary separation of the starting substances from the reaction mixture at 160°/ $1.5 \cdot 10^{-2}$ mm Hg and molecular distillation at 185°/ $1.5 \cdot 10^{-2}$ mm. It was a colorless syrupy liquid. Yield 55%. n_D^{20} 1.5373; d_4^{20} 1.1927. *MR* found 52.30; calculated 51.45.

Found, %: P 15.10. Calculated, %: P 15.65

Carrying out the homopolytransesterification reaction. The apparatus for carrying out this reaction was described earlier ([1,2]). For the reaction, 0.1 mole of the ester of oxymethylphosphinic acid was taken. From the amount of liberated

the amount of alcohol being distilled off was used to calculate the degree of completion of the reaction, and its dependence on time was established.

The polyester was purified by dissolution in dioxane, followed by precipitation with diethyl ether and drying in a vacuum oven at 100°. The molecular weight was determined by the cryoscopic method.

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Note: Figure translations are in progress. See original paper for figures.