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Corresponding Member of the USSR Academy of Sciences A. N. Pudovik, A. P. Rakov

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Abstract

Full Text

CHEMISTRY

Corresponding Member of the USSR Academy of Sciences A. N. Pudovik, A. P. Rakov

ON THE QUESTION OF THE THERMAL REARRANGEMENT OF COMPLETE ESTERS OF PHOSPHOROUS ACID WITH SATURATED RADICALS

As was shown by A. E. Arbuzov in 1905, complete esters of phosphorous acid rearrange into esters of alkylphosphinic acids in the presence of alkyl halides ([1]). In the case of esters of phosphorous acid with unsaturated radicals, the rearrangement can take place also in the absence of alkyl halides—by a thermal route. Thus, we have recently shown that allyl dialkyl esters of phosphorous acid, when heated to 180–200°, undergo thermal rearrangement into dialkyl esters of allylphosphonic acids ([2]). An analogous rearrangement under considerably milder conditions also occurs in the case of propargyl esters of phosphorous acid ([3–5]). When substituent groups are present at the α- or γ-carbon atoms of the unsaturated radical, the rearrangement is accompanied by inversion of the radicals. It is most probable that rearrangements of this type proceed by a mechanism of cyclic electron transfer. They have much in common with the Claisen rearrangement; the role of the double bond in esters of phosphorous acid is performed by the unshared electron pair of the phosphorus atom.

Therefore we considered it possible to regard them as thermal rearrangements of the "pseudo-Claisen" type ([6]).

In light of the investigations carried out, it seemed of interest to study the possibility of thermal rearrangement of complete esters of phosphorous acid with saturated radicals. In the literature there are a number of works in which the thermal rearrangement or thermal decomposition of esters of phosphorous acid with saturated radicals is described.

Zimmermann ([7]), as early as 1875, noted that when triethyl phosphite is heated in a sealed tube for 10 hours at 250°, phosphorous hydrogen is formed, detected by a qualitative reaction with silver nitrate. Zimmermann suggested that the decomposition of triethyl phosphite occurs with the formation of phosphorous acid and phosphine. However, as was shown by A. E. Arbuzov, Zimmermann, Ihne ([8]), and other investigators of that time had in their hands not pure esters of phosphorous acid, but mixtures of them with incomplete esters of phosphorous acid and esters of phosphoric acid; therefore the results obtained by them cannot

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be considered reliable.

The scheme proposed by Zimmermann was used in the work of Sanin and Ulyanova ([9]), who studied the thermal decomposition of *n*-tributyl phosphite and trioctadecyl phosphite. The authors, unfortunately, do not report on the purity of the phosphites used in the reaction. The phosphites were heated in a reactor under a weak stream of nitrogen. In addition to phosphoric acid and phosphine, they established the formation of butylene and, correspondingly, octylene.

In contrast to the authors mentioned, Simon and Schulze ([10]) found that triethyl phosphite, when heated in a sealed tube at 250° for 24 hours, is rearranged to a significant extent into the diethyl ester of ethylphosphinic acid (up to 70%).

Such a substantial difference in the results obtained by the cited authors prompted us first of all to repeat the experiments described by them. Trimethyl phosphite, triethyl phosphite, *n*-tripropyl phosphite, triisopropyl phosphite, and *n*-tributyl phosphite were heated in sealed tubes in an atmosphere of carbon dioxide.

On 12-hour heating at 230–250°, trimethyl phosphite (b.p. 109–110°; d_4^{20} 1.0581; n_D^{20} 1.4088) remained unchanged. As a result of 12-hour heating at 260–270°, triethyl phosphite (b.p. 48.5°/12 mm; d_4^{20} 0.9565; n_D^{20} 1.4134) also was recovered almost completely from the reaction; in the residue after distillation of the phosphite, an insignificant amount of red phosphorus was detected. Particularly illustrative is the experiment on heating triethyl–

Table 1

Composition of the reaction mixture in moles: triethyl phosphite	Composition of the reaction mixture in moles: diethyl phosphorous acid	Ratio of reagents	Experimental conditions: temperature, °C	Experimental conditions: time, h	Recovery of phosphite, %	Yield of diethyl ester of ethylphosphinous acid, %
0.1	0.100	1 : 1	265–267	5	13.3	75.9
0.1	0.050	2 : 1	265–267	5	59.7	30.2
0.1	0.025	4 : 1	265–267	5	84.3	15.0
0.1	0.010	10 : 1	265–267	12	76.1	13.3
0.1	0.009	11 : 1	270–300	30	9.3	78.0

phosphite at 270–310° for 70 h–95% of the phosphite was recovered; in the residue there was a small amount of red phosphorus and resin. *n*-Tripropyl phosphite remained unchanged on heating for 5 h at 275–280° (b.p. 92–93°/14

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mm; d_4^{20} 0.9266; n_D^{20} 1.4264), as did triisopropyl phosphite (b.p. 83°/30 mm; d_4^{20} 0.8992; n_D^{20} 1.4135). On heating triisopropyl phosphite for 5 h at 280-290°, considerable decomposition occurred, with evolution of a large amount of gas and red phosphorus and with formation of resinous products.

n-Tributyl phosphite behaved differently from the others (b.p. 119.5-120.5°/10 mm; d_4^{20} 0.9150; n_D^{20} 1.4325). As a result of 5-hour heating at 277-282°, along with unchanged phosphite, dibutyl ester of butylphosphinous acid was isolated in yields up to 35%, as well as a rather considerable amount of butene-2. The latter was identified by conversion into 2,3-dibromobutane (b.p. 159.5-160°; d_4^{20} 1.7846; n_D^{17} 1.5157), the constants of which coincide with those reported in the literature. In the IR spectrum of the reaction mixture of the main experiment before distillation, there were absorption bands of weak intensity characteristic of the P—H bond, which indicates the presence in it of dibutyl phosphorous acid.

On the basis of the experiments presented, we came to the conclusion that full esters of phosphorous acid with lower radicals are not capable of thermal rearrangement into the corresponding esters of alkylphosphinous acids. As a result of analysis of the data obtained by us and of the experiments of previous investigators, we came to the conclusion that the reason for such a sharp discrepancy in the results is the purity of the phosphites used for the reaction. In our experiments we used pure phosphites, free from dialkylphosphorous acids. For this purpose, phosphites obtained by the Milobendzkii method (from phosphorus trichloride and absolute alcohol in ether solution in the presence of a base), in order to remove the dialkylphosphorous acids contained in them in small amount (up to 10%), were heated for several hours over sodium in ether solution. The reaction mixtures were then distilled in vacuo (11).

In the investigations cited above (9, 10), the phosphites, obtained by the Milobendzkii method (12) or by Yené (8), were not subjected to additional treatment with sodium and, consequently, contain impurities of acid esters. We have established that acid esters of phosphorous acid under the conditions

prolonged heating with phosphites, at high temperature, react with them with formation of esters of alkylphosphinic acids. Table 1 gives the results of experiments on heating pure triethyl phosphite with various amounts of diethyl phosphorous acid.

The greater the amount of diethyl phosphorous acid in the reaction mixture, and the higher the temperature and the heating time, the higher the yield of the diethyl ester of ethylphosphinic acid that is formed (b.p. 87-87.5°/16 mm; d_4^{20} 1.0230; n_D^{20} 1.4165). On heating tripropyl phosphite with *n*-dipropylphosphorous acid for 5 h at 261-265°, the dipropyl ester of propylphosphinic acid was obtained in 46% yield (b.p. 118.5-119°/10 mm; d_4^{20} 0.9805; n_D^{20} 1.4251). The IR spectra of the esters obtained are completely identical with the spectra of esters obtained by the method of A. E. Arbuzov. We believe that the reaction between neutral and acid phosphites containing a labile hydrogen atom proceeds according to the scheme of the Arbuzov rearrangement:

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$$(RO)_3P + \begin{matrix} H \\ P(OR)_2 \\ O \end{matrix} \rightarrow [(RO)_3PH]^+P(\overline{O}R)_2 \rightarrow R{-}P(=O)(OR)_2 + (RO)_2POH.$$

When the radicals in the neutral and acid phosphites are the same, the latter performs the function of a catalyst of the reaction.

To verify the correctness of our conclusions, we carried out the reaction between triethyl phosphite and the acidic ethyl ester of phenylphosphonous acid. An equimolecular mixture of the reagents was heated for 4 h at 248-270°. As a result, the ethyl ester of ethylphenylphosphinic acid was obtained in 27% yield.

On the basis of a study of the IR spectra of the lower-boiling fractions, we came to the conclusion that they contain diethyl phosphorous acid, the diethyl ester of ethylphosphinic acid, and triethyl phosphate. The results obtained are not unexpected. Examples are known from the literature of the interaction of neutral phosphites with other substances possessing a labile hydrogen atom: mineral ([13]) and organic ([14]) acids, and aliphatic alcohols ([15]). We also carried out a series of experiments on heating unpurified trimethyl and triethyl phosphites, obtained by the Milobendzkii method and containing up to 10% acid esters, under conditions close to those described by Simon and Schulze. The dimethyl ester of methylphosphinic acid and the diethyl ester of ethylphosphinic acid, respectively, were obtained. Their yields in different experiments, depending on the time and temperature of heating, ranged from 15 to 90%.

It follows from the results obtained that the data of Simon and Schulze on the possibility of thermal isomerization of neutral esters of phosphorous acid with saturated radicals do not correspond to reality. The inability of neutral phosphites with saturated radicals to undergo thermal isomerization into esters of alkylphosphinic acids is evidently explained by the difficulty of a three-center electron transfer owing to steric hindrance and the absence in the ether radical of an active carbon center capable of accepting electrons from the phosphorus atom. The latter reason probably also excludes the possibility of the rearrangement proceeding by an intermolecular mechanism with a six-center transition state.

Of particular interest is the behavior of pure *n*-tributyl phosphite on heating. In this case, as already noted above, a considerable amount of the dibutyl ester of butylphosphinic acid and butylene-2 is formed. According to the IR spectrum, the first fractions contain dibutyl phosphorous acid (intense absorption bands at 2412 and 1253 cm^{-1}, characteristic of P–H and P=O). A similar

The same picture is obtained also on heating *n*-tributyl phosphite in the presence of hydroquinone.

As is known from work (16), esters of phosphinic acids, when boiled, undergo gradual decomposition with liberation of an olefin and formation of phosphinic

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acid. This reaction proceeds most readily for esters having tert-butyl radicals; with decreasing branching and size of the radicals, its rate falls considerably. Apparently, in our case the initial reaction on heating *n*-tributyl phosphite is the formation of *n*-dibutylphosphorous acid. It seems to us more probable that this and similar reactions proceed by the mechanism of a five- or six-center cyclic electron transfer with direct participation therein of the phosphorus atom (A) for phosphites and of the $P = O$ bond in esters of phosphinic acids (B), and not by a four-

(A) (B) (V)

center process with participation of the ether oxygen (V), as is proposed in work (16). The role of the $P = O$ group in scheme A is fulfilled by the phosphorus atom with its unshared electron pair (17). It is quite probable that an analogous reaction can also occur for phosphites with lower radicals, but at a higher temperature. Thus, according to the data of work (16), decomposition of the diethyl ester of hexylphosphinic acid with liberation of ethylene begins only at 340°. The behavior of phosphites above 300° has not yet been studied by us.

With further interaction of *n*-dibutylphosphorous acid with tributyl phosphite, the dibutyl ester of butylphosphonic acid is formed. It is possible that under certain temperature conditions further dealkylation of dibutylphosphorous acid to phosphorous acid will occur; under the conditions of the experiment the latter undergoes decomposition with formation of phosphoric acid and phosphine. Such a direction of the course of the reaction is discussed as one of the possibilities in the work of Sanin and Ul' yanova (9). This question, however, requires additional study.

We shall report separately on an investigation of the behavior at elevated temperatures of complete phosphites with higher radicals, esters of phosphonous acids, and acid esters of phosphorous acid.

Kazan State University
named after V. I. Ul' yanov-Lenin

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