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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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STUDY OF THE INTERACTION OF ESTERS OF PHOSPHOROUS ACID WITH ALKYL HALIDES BY METHODS OF PHYSICO-CHEMICAL ANALYSIS

The mechanism of the A. E. Arbuzov rearrangement has been the subject of study for 50 years. A. E. Arbuzov ⁽¹⁾ considers that the rearrangement of phosphites into esters of alkylphosphinic acids is a two-stage process with the formation of an intermediate product of the phosphonium type. For aromatic phosphites such a mechanism was demonstrated experimentally by him. There is an opinion that for aliphatic phosphites the intermediate products immediately decompose spontaneously and, as such, are not capable of existence ⁽²⁾. A number of investigators, however, believe that the rearrangement can proceed by another mechanism, without formation of the product of addition of the alkyl halide to the phosphite ^(3,4).

In the present communication we set forth data obtained by us in studying the A. E. Arbuzov rearrangement by methods of physicochemical analysis. The principal task of the investigation was to determine the possibility of using the composition–property diagram for studying the question of the formation of an intermediate product in the rearrangement of aliphatic phosphites into esters of phosphinic acids.

We studied the interaction of triethyl phosphite with ethyl iodide and ethyl bromide and with dibromodiethyl ether, as well as of triphenyl phosphite with methyl iodide and ethyl iodide at various temperatures. Measurements of the constants were carried out at 20° after preliminary heating of the mixtures in thermostats at the specified temperatures. The measurement temperature of 20° was chosen because of the volatility of one of the components.

Fig. 1

Figures 1 and 2 present data on measurements of the constants on the composition–property diagram for the system triethyl phosphite–ethyl iodide at various

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

temperatures.

The curves of refractive index and density are convex toward the composition axis and, consequently, do not reflect chemical interaction. The isotherms of specific electrical conductivity χ , natural compression D_n , and, especially, viscosity η , indicate interaction of the components. For the isotherms η , D_n , and χ , a shift of the maximum to the left with increasing temperature is characteristic.

The isotherms listed, reflecting the chemical interaction between the components, do not make it possible to draw a conclusion about the absence or formation of an intermediate product. Evidently, the composition of the system is more complex, and the intermediate product, if it is formed, partially decomposes into alkyl halide and phosphinous acid ester.

Fig. 2

Of considerable interest are the results of studying the system triethyl phosphite— α, β -dibromodiethyl ether. According to V. S. Abramov's data (⁵), the interaction of the components for this system begins already at room temperature and leads to the formation of the intermediate product of the A. E. Arbuzov rearrangement.

As follows from Figs. 3 and 4, the isotherms n_D^{20} and d^{20} , as in the case of ethyl iodide, are convex toward the composition axis; however, the deviation from the additive straight line is considerably smaller here, especially for the density isotherm, whose convexity is slight.

The deviation of the specific-volume isotherm Δv_{sp} and the isotherm of natural compression D_n , calculated according to Bieron, clearly indicate a maximum of compression for a mixture of composition 1 : 1. The viscosity isotherm is distinguished by a somewhat peculiar form. Its S-shaped appearance, with the presence of a singular-type inflection point at a component ratio of 1 : 1, indicates not only interaction of the components but also association of one of the components, evidently α, β -dibromodiethyl ether.

Fig. 3

Fig. 4

Figure 4: Fig. 4

Fig. 4

Thus, the data of the composition–property diagrams for the system triethyl phosphite– α , β -dibromodiethyl ether confirm the presence of chemical interaction in the system and, together with the data obtained by V. S. Abramov ⁽⁵⁾, serve as proof of the formation of an intermediate addition product in the process of rearrangement of triethyl phosphite into the ester of ethoxybromophosphinous acid.

The fact that the composition–property diagrams obtained reflect, in the present case, the formation of an intermediate product, and not of the final rearrangement product, is indicated by the deviation of the viscosity of the system from additivity, which for the equimolecular mixture is 2 times greater than the deviation for the triethyl phosphite–ethyl iodide mixture in a 1 : 1 ratio after heating at 50°.

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CITED LITERATURE

1. A. E. Arbuzov, *On the Structure of Phosphorous Acid and Its Derivatives*, Dissertation, 1905.
2. G. M. Kosolapoff, *Organophosphorus Compounds*, N. Y., 1950, p. 122.
3. P. Rumpf, *Bull. Soc. Chim.*, No. 3-4, 128C (1951).
4. B. E. Smith, A. Burger, *J. Am. Chem. Soc.*, **75**, 5891 (1953).
5. V. S. Abramov, G. Karp, *DAN*, **91**, 1095 (1953); *ZhOKh*, **24**, 1823 (1954).

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