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M. G. Gonikberg, I. Z. Fainshtein

Investigation of the Effect of Pressure on the Rate of A. E. Arbuzov Reactions

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High pressure substantially accelerates liquid-phase reactions in which the stage determining the rate of the overall process involves the interaction of two or more particles (in particular, addition reactions, nucleophilic substitution, polymerization, etc.). In addition, the effect of pressure on the reaction rate also depends on the solvation of the transition state. If the transition state is solvated by solvent molecules to a greater extent than the initial particles, then such a reaction is accelerated by pressure, and vice versa ([1]).

Pressure affects the rate of isomerization reactions differently depending on their mechanism. Thus, for example, the cis–trans isomerization of 1,2-dichloroethylene, catalyzed by iodine atoms, is accelerated when the pressure is raised ([2]). In the rate-determining stage of this reaction, an iodine atom interacts with a dichloroethylene molecule. On the other hand, the rearrangement of N-chloroacetanilide into *o*- and *p*-chloroacetanilides in aqueous solution (catalyst HCl) is retarded by pressure ([3]). The transition state in this reaction is less solvated than the initial ions $C_6H_5NHClCOCH_3$ and Cl^- ([4]). The effect of pressure on the rate of the A. E. Arbuzov rearrangement, as far as we know, has not previously been studied. At present it may be considered established that this reaction proceeds in two stages with the formation of intermediate addition products of alkyl halides to phosphites. Therefore one could expect an accelerating effect of pressure in Arbuzov reactions.

In the present work we studied the effect of pressure on the course of the rearrangement

$$(C_2H_5O)_3P \xrightarrow{C_2H_5J} (C_2H_5O)_2(C_2H_5)PO, \qquad (1)$$

as well as the reaction

$$(C_2H_5O)_3P + (CH_3)_2CHJ \rightarrow (C_2H_5O)_2PCH(CH_3)_2 + C_2H_5J. \qquad (2)$$

Fig. 1. Rearrangement of triethyl phosphite at 80°: 1—at atmospheric pressure; 2—at a pressure of 2000 kg/cm^2

Figure 1: Fig. 1. Rearrangement of triethyl phosphite at 80°: 1—at atmospheric pressure; 2—at a pressure of 2000 kg/cm^2

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The starting triethyl phosphite was synthesized by the action of phosphorus trichloride on absolute ethyl alcohol in the presence of pyridine ([5]), and after distillation on a rectification column of 20 theoretical plates was characterized by the following constants: b.p. 155-156°/750 mm; d_4^{20} 0.9614; n_D^{20} 1.4139 (according to the literature: b.p. 154.5-155.5°/755 mm ([6]); d_4^{20} 0.9630 ([7]); $n_D^{17.5}$ 1.4140 ([8]); n_D^{20} 1.4135 ([9])). Ethyl iodide and isopropyl iodide were distilled on a column of the same efficiency and were characterized by constants close to those reported in the literature.

Rearrangement of triethyl phosphite. Experiments on the rearrangement of triethyl phosphite were carried out in a steel reactor of capacity $\sim$ 200 ml with a multiplier and a device for withdrawing samples during the process.

of the reaction (10). The reactor was thermostated; the experiments were carried out at 80$\pm$0.2°. Analysis of the samples for the content of unreacted phosphite in them was performed by titration with a 0.1 N solution of bromine in methanol; the excess bromine was determined iodometrically. This method of analysis was tested by us on artificial mixtures of triethyl phosphite, the product of its isomerization, and ethyl iodide; it gave quite satisfactory results.

A solution of triethyl phosphite and ethyl iodide in toluene (in a molar ratio of 1 : 1 : 6) was placed in the heated reactor, after which the pressure was raised with the aid of a multiplier. The results of experiments at atmospheric pressure and at 2000 kg/cm^2 are shown in Fig. 1. From the kinetic curves obtained, the rate constant of the pseudomonomolecular reaction was calculated; it proved to be $\sim$ 0.02 h^{-1} at atmospheric pressure and $\sim$ 0.27 h^{-1} at 2000 kg/cm^2. If it is assumed that the values found for the rate constants include the concentration of ethyl iodide and if the compressibility of the solution is taken into account (11), then it turns out that increasing the pressure from atmospheric to 2000 kg/cm^2 leads to an increase in the rate constant of reaction (1) by almost a factor of 12.

Fig. 1. Rearrangement of triethyl phosphite at 80°: 1—at atmospheric pressure; 2—at a pressure of 2000 kg/cm^2.

Interaction of triethyl phosphite with isopropyl iodide. This reaction was first carried out by us in a sealed ampoule at 100°. A mixture of triethyl phosphite (5.1 g) and isopropyl iodide (10.4 g) reacted over 8 h only to the extent of 11% (as found by titration of the phosphite). Distillation of the reaction products showed the presence, in the low-boiling fractions, of ethyl iodide in an

amount of ~ 0.3 g. Comparison of the rearrangement of triethyl phosphite and its interaction with isopropyl iodide shows that the second reaction proceeds considerably more slowly than the first. As is known from the work of A. E. Arbuzov (12), triethyl phosphite in an equimolecular mixture with ethyl iodide undergoes complete rearrangement at 100° in only 5 h. B. A. Arbuzov and A. V. Fuzhenkova (13) found that, under thermographic analysis conditions, the interaction of triethyl phosphite with ethyl iodide begins to be observed at a significantly lower temperature (108°) than its interaction with isopropyl iodide (166°). Apparently, this is connected with the greater steric hindrance of the latter reaction. It could be expected that high pressure would accelerate the reaction of triethyl phosphite with isopropyl iodide to an even greater extent than the rearrangement of triethyl phosphite in the presence of ethyl iodide. This assumption is based on the observation that the more sterically hindered a reaction is, the more strongly it is accelerated with increasing pressure (14, 15).

Further experiments were carried out by us in an ultrahigh-pressure multiplier with internal electric heating (16). A mixture of the starting substances (molar ratio $(C_2H_5O)_3P : (CH_3)_2CHJ = 1 : 2$), in an amount of ~ 3 g, was placed in a thoroughly washed and dried lead ampoule with a branch tube, which was then sealed. The ampoule, equipped with a pocket for a thermocouple, was placed inside an electric furnace into the channel of the high-pressure vessel filled with isopentane. The temperature of the cold junction of the thermocouple was measured by a copper resistance thermometer located in the lower part of the high-pressure vessel; the pressure was measured with a manganin manometer. In the channel of the high-pressure vessel, a pressure of ~ 12000 kg/cm^2 was first created. Then the electric heating was switched on, and the temperature slowly rose. Upon reaching $\sim 90°$, in all experiments spontaneous

a spontaneous rise in temperature; the junction of the thermocouple in the ampoule pocket was heated for 10–20 sec to $\sim 120°$, after which the temperature again fell to $\sim 90°$. A qualitative test with a $0.1\,N$ solution of bromine in methanol showed the complete absence of trivalent phosphorus in the reaction products. The products from 5 experiments were combined and distilled in an amount of 12.5 g. The following fractions were collected: fraction 1, b.p. 75–88°/750 mm (a mixture of ethyl iodide with isopropyl iodide), 7.5 g; fraction 2, b.p. 51–57°/1 mm, 3.4 g; fraction 3, b.p. 87–94°/1 mm, 0.4 g; residue, 0.9 g. Fractions 2 and 3 were again distilled in vacuo into two fractions: fraction 1, b.p. 73–77°/7 mm, 2.7 g; fraction 2, b.p. 77–78°/7 mm, 0.7 g; residue, 0.2 g. Fraction 1, in its composition, corresponded to the diethyl ester of isopropylphosphinic acid:

Found, %:	C 46.47, 46.52;	H 9.37, 9.43;	P 16.83, 17.14
$C_7H_{17}O_3P$. Calculated, %:	C 46.67;	H 9.50;	P 17.20

Fraction 1 was then distilled at atmospheric pressure; b.p. 207–210°/753.6 mm; d_4^{20} 0.9951; n_D^{20} 1.4154.

Thus, in experiments at a pressure of 12000 kg/cm^2, the interaction of triethyl phosphite and isopropyl iodide, with formation of the diethyl ester of isopropylphosphinic acid, proceeds very rapidly already at a temperature of 90°, while diethyl ethylphosphonate is practically absent from the reaction products.

The results obtained in the present work indicate that high pressure accelerates the Arbuzov reactions to a very considerable extent. It is possible that, under high pressure, it will also be possible to carry out spatially hindered reactions of esters of phosphorous acid with haloalkyls that do not undergo the Arbuzov rearrangement under ordinary conditions.

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

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