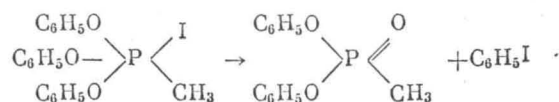


EFFECT OF PRESSURE ON THE THERMAL DECOMPOSITION
OF METHYLTRIPHENOXYPHOSPHONIUM IODIDE

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Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 8,
pp. 1469-1471, August, 1965
Original article submitted November 20, 1964

In our studies [1, 2], it was demonstrated that pressure extremely substantially accelerates the Arbuzov reaction; moreover, it was hypothesized that the observed effect is due to the influence of pressure on the first step of the reaction. An unambiguous answer to this question would necessitate, at least a qualitative determination of the influence of pressure on the second step of the reaction; this was the purpose of this work. In it we studied the thermal decomposition of methyltriphenoxyphosphonium iodide—the stable intermediate addition product in the reaction of rearrangement of the phenyl ester of phosphorous acid in the presence of methyl iodide [3]



EXPERIMENTAL SECTION

Methyltriphenoxyphosphonium iodide was produced by heating a mixture of triphenyl phosphite and methyl iodide in a sealed glass ampoule at 130° for 2.5 h [4, 5]. After two recrystallizations from a mixture of thoroughly dried dichloroethane and ether, we obtained white crystals with m. p. 140°. Literature data [4]: m.p. 130°; [6]: m. p. 146°. Found: I 28.45; 28.30; 28.17%. $\text{C}_{19}\text{H}_{18}\text{O}_3\text{PI}$. Calculated: I 28.10%.

Experiments on thermal decomposition were conducted at $200 \pm 0.2^\circ$ at the saturated vapor pressure of the initial compound, as well as at a hydrostatic pressure of 2000 kg/cm^2 . In the first case, the substance was placed in a glass ampoule, which was then sealed. Experiments at high pressure were conducted in a steel vessel specially designed for this purpose, into which a Teflon ampoule with the starting material was placed (the construction of the ampoule is described in [7]). An initial oil pressure of 820 kg/cm^2 was created in the vessel with a NZhR pump, after which the vessel was placed in a thermostat heated to the temperature of the experiment; then the oil pressure was raised to 2000 kg/cm^2 in a period of several minutes, and remained constant during the entire experiment (19 h). Then the thermostat was cooled by passing cold water through a coil placed in it. All the operations with the starting material, as well as opening of the glass and Teflon ampoules, were performed in a stream of dry nitrogen. In the experiments in a glass ampoule, the amount of substance loaded was $\sim 11 \text{ g}$, and in the Teflon ampoule $\sim 8 \text{ g}$. The reaction products were also distilled in a stream of dry nitrogen; the fraction with b. p. $71-72^\circ$ (14 mm), containing iodobenzene with a small admixture of phenol ($\sim 1\%$ by weight of the starting material) was distilled off. The iodobenzene and phenol contents in this fraction were determined according to the coefficient of refraction from a calibration curve " n_D^{20} versus percent by weight phenol." After distillation of the indicated fraction, the residue was treated with absolute ethanol; under these conditions all the unreacted methyltriphenoxyphosphonium iodide is converted to an ester of methylphosphinic acid, with the simultaneous formation of ethyl iodide and phenol [3]. Then the mixture of ethyl iodide and unreacted ethanol was distilled off, after which the phenol was distilled off under vacuum; the fraction of unreacted initial compound was judged according to the amount of phenol. In the thermal decomposition of methyltriphenoxyphosphonium iodide, certain side reactions also take place—resinification, isolation of iodine, and formation of small amounts (1-2% by weight) of benzene. The experimental results are summarized in the Table.

Thermal Decomposition of Methyltriphenoxyphosphonium Iodide at 200° ($\tau = 19$ h)

Pressure	Composition of reaction products, mol. % of initial compound			
	Iodobenzene	Initial compound*	Total	Products of side reactions†
Saturated vapor pressure	23.2	66.0	89.2	10.8
The same	23.5	67.5	91.0	9.0
2000 kg/cm ²	17.7	65.2	82.9	17.1
2000 kg/cm ²	17.4	61.5	78.9	21.1

* According to yield of phenol.

† By difference; this figure includes the distillation loss (2-3% by weight).

The Table data indicate that increasing the pressure leads to a certain decrease in the yield of iodobenzene and an increase in the yield of side products of the reaction; the amount of unreacted starting material remains practically unchanged.

Discussion of the Experimental Results

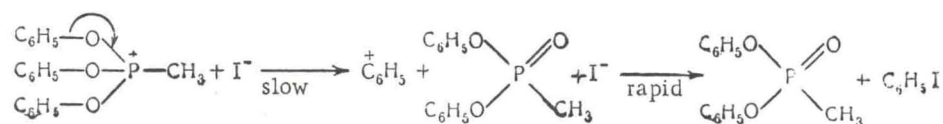
The results of this work confirm the hypothesis [1, 2] that the substantial accelerating effect of pressure on the Arbuzov reaction is related not to the second, but to the first step of the reaction. Here it may be a matter both of an increase in the rate constant of the first step and of a shift of the equilibrium toward the formation of the intermediate addition product in the first stage of the reaction.

According to the theory of the transition state [8], the dependence of the reaction rate constant on the pressure is determined by the sign and magnitude of the volume effect of activation Δv^\ddagger

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\Delta v^\ddagger / RT, \quad (1)$$

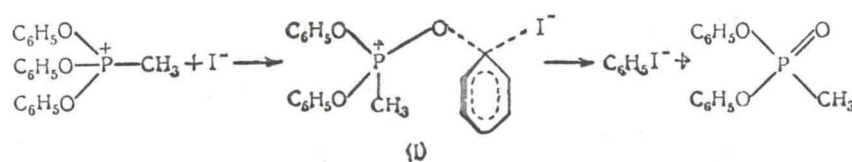
The data obtained in this work permit us to conclude that in the reaction studied, the process of activation is accompanied only by a negligible change in the volume.

It is noted in the literature [9] that the thermal decomposition of the addition product in Arbuzov reactions might occur both according to a monomolecular and according to a bimolecular reaction. In the case of an S_N1 mechanism, the reaction proceeds according to the scheme



Here, in the slow step of the reaction, two particles are formed from one (in the activated complex, the bond undergoing cleavage is stretched out), which should have led to a certain increase in the volume, i. e., to a small positive volume effect of activation. However, the $C_6H_5^+$ ion formed is smaller than the initial ion; this is responsible for the somewhat greater electrostatic interaction of the activated complexes with the surrounding medium in comparison with the initial ions, and should thereby lead to a certain decrease in the volume. Obviously, the value of the summary volume effect of activation should be small, and its sign is difficult to predict.

Now let us consider the occurrence of the reaction according to an S_N2 mechanism:



In this case the volume effect of oxidation, it might seem, should possess a negligible negative value—one particle—the activated complex I—is formed from two particles [10]. However, the activated complex is less polar than the original ions, since it is intermediate between these ions and the reaction product. As a result, the electrostatic interactions of the activated complex with the surrounding medium will be smaller than those of the original ions; this should lead to some increase in the volume. Thus, in this case also we might expect a small volume effect of activation of either sign.

The analysis cited above shows that the results of this investigation agree both with monomolecular and with bimolecular schemes of the mechanism of the second step of the Arbuzov rearrangement.

SUMMARY

1. Raising the pressure from 2000 kg/cm² exerts a negligible effect upon the rate of the thermal decomposition of methyltriphenoxyphosphonium iodide at 200°. This result permits us to conclude that the previously detected substantial accelerating effect of pressure on the Arbuzov reaction is connected not with the second, but with the first step of this reaction.

2. The effect of pressure found does not permit a selection between the monomolecular and bimolecular schemes of the mechanism of the thermal decomposition of methyltriphenoxyphosphonium iodide.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.
