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 $\Delta v^{\neq}$

$$(\partial \ln k / \partial P)_T = -\Delta v^{\neq} / RT. \tag{1}$$

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
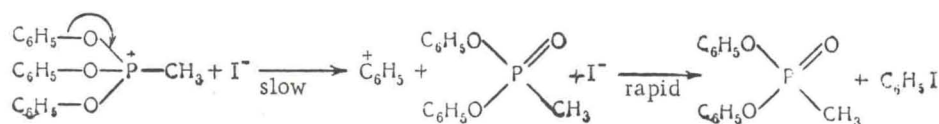
Here, in the slow step of the reaction, two particles are formed from one (in the activated complex, the bond undergoing cleavage is stretched out), which should have led to a certain increase in the volume, i. e., to a small positive volume effect of activation. However, the $C_6H_5^+$ ion formed is 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: