STUDY OF THE REACTIONS OF PHOSPHOROUS ESTERS
WITH ALKYL HALIDES BY THE THERMOGRAPHIC METHOD

COMMUNICATION 2. REACTIONS OF ALIPHATIC PHOSPHITES

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We have shown [1] with the aid of the thermographic method that in the case of aromatic and mixed
aliphatic-aromatic phosphorous esters the Arbuzov rearrangement proceeds in two stages, which are revealed as
two exothermic effects in the thermograms for reaction between these esters and alkyl iodides or bromides.

Special interest is presented by the study of the rearrangement of aliphatic phosphorous esters, for which
the intermediate products have not been isolated. It is therefore important to determine whether the thermo-
graphic method can demonstrate the two-stage character of the Arbuzov reaction in the case of aliphatic phos-
phites. It follows from the results of our investigations [1] that the stability of the intermediate products falls
along the series of phosphorous esters \( P(OC_2H_5)_3 \rightarrow (C_6H_5O)_2P \rightarrow OC_2H_5 \rightarrow C_6H_5OP \rightarrow (OC_2H_5)_2 \), and therefore the
possibility of detecting the two-stage character of the rearrangement by the thermographic method is not inde-
pendent of the rate of heating. Whereas the first two esters of this series each give two exothermic effects both
with rapid (5-6°/minute) and with slow (0.3-0.4°/minute) heating, in the case of the third phosphorous ester,
\( C_6H_5OP(OC_2H_5)_2 \) two effects can be detected only if the furnace is heated slowly.

As the last in this series of phosphorous esters is the fully aliphatic phosphite triethyl phosphite \( (OC_2H_5)_3 \),
it may be supposed that for aliphatic phosphites the two-stage character of the reaction will be detectable only
when heating is slow. To resolve this question we made a thermographic study of the reaction of aliphatic phos-
phites with alkyl halides, the esters examined being trimethyl and triethyl phosphites. It was found that in the
reaction of these esters with alkyl halides proceeding at a rate of heating of 4-5°/minute only one exothermic
effect was generally observed. As in the case of aromatic phosphites, the temperature at which the reaction
between aliphatic phosphites and alkyl halides begins and continues depends on the nature of the halogen, the
structure of the alkyl halide, and the place of the alkyl halide in the homologous series: with rise in molecular
weight, the temperature at which the Arbuzov reaction occurs rises (Tables 1 and 2). For the systems formed by
triethyl phosphite with methyl iodide, benzyl iodide, 1,2-dibromoethyl ethyl ether, 1,2-dichloroethyl ethyl ether,
and 2,3-dibromopropionitrile, two exothermic effect were recorded on the thermograms (Fig. 1).

The presence of only one exothermic effect in several cases could be explained on the view that, at the
rates of heating used (4-5°/minute), the reaction was so rapid that the two stages of the reaction could not be
registered separately on the thermograms, but merged into a single exothermic effect.

It was, in fact, found that with slow heating (0.3-0.4°/minute) two exothermic effects appeared on the
thermograms of the following equimolecular mixtures (Fig. 2 and 3):

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\begin{align*}
P(OC_2H_5)_3 & \rightarrow C_6H_5I; \\
P(OC_2H_5)_3 & \rightarrow C_6H_5Br; \\
P(OC_2H_5)_3 & \rightarrow C_6H_5CH_2Br; \\
P(OC_2H_5)_3 & \rightarrow CH_2BrCOOC_2H_5; \\
P(OC_2H_5)_3 & \rightarrow CH_2CHBrCOOC_2H_5; \\
P(OC_2H_5)_3 & \rightarrow CH_2JCH_2COOC_2H_5; \text{etc.}
\end{align*}
\]
To resolve the question of whether the two effects belong to the two stages of the Arbuzov rearrangement, we measured the viscosity of each mixture after it had been heated to the temperature for the first effect and also after it had been heated to the temperature for the second effect. According to the structure of the intermediate product, its viscosity should be greater than that of the final product. Hence, the viscosity of the mixture that had been heated to the temperature for the first effect should be higher than the viscosity corresponding to the second effect. The results of the measurements, however, showed the reverse: the viscosity of the mixture corresponding to the first effect is lower than that corresponding to the second. It is therefore difficult to conclude that the two effects reflect two stages of reaction, for the nature of these effects can be interpreted differently if it is supposed that the first effect reflects the whole reaction including its first and second stages. The second effect can then be explained either on the view that the final product reacts in some way with the alkyl halide liberated in the reaction \((\text{RO})_2 P \rightarrow R + \text{RHal}\), or on the view that at the point corresponding to the first effect the rearrangement does not go to completion, but residual phosphorous ester reacts further, not with the alkyl halide originally taken for reaction, but with the alkyl halide liberated as a result of the first reaction.

However, there is an objection to each of these views: on the one hand, the thermograms given by the isomerized product \((\text{C}_2\text{H}_5)P - (\text{OC}_2\text{H}_5)_2\) in admixture with ethyl iodide, with ethyl bromide, and with benzyl iodide show no evidence of interaction between the components, and on the other hand, the amounts of the components were taken in strictly equivalent proportions. There would seem, therefore, that there is no foundation for the view that the phosphorous ester does not react fully with the alkyl halide \(\text{RHal}\) taken for reaction, but reacts until there is an accumulation of the alkyl halide \(\text{RHal}\) liberated and the whole system attains the temperature at which reaction between the phosphorous ester \(\text{P(OR)}_3\) and the liberated alkyl halide \(\text{RHal}\) is possible. Also, the temperature range corresponding to the first and second effects is wide, so that it would be possible to isolate the intermediate addition product. However, this has not been done. These considerations indicate the necessity for further study of the nature of the two exothermic effects in the above reactions.

Reaction between the components is again accompanied by two exothermic effects in the case of the mixtures of triethyl phosphite with 1,2-dichloroethyl ethyl ether and with 1,2-dibromoethyl ethyl ether. However, whereas the viscosity of the mixture corresponding to the first effect is lower than that corresponding to the second effect in the case of the above-cited mixtures of triethyl phosphite with an alkyl halide or ester of a halo acid, the reverse is true for mixtures of triethyl phosphite with 1,2-dichloro- or 1,2-dibromo-ethyl ether (Table 3).

This is in accord with the view that the first effect is due to the formation of the intermediate product. Separate experiments were carried out on the change in the viscosity of an equimolecular mixture of triethyl phosphite and 1,2-dibromoethyl ethyl ether with rise in the temperature of the heat treatment (the duration of the heating was the same for all temperatures). The results showed that the viscosity of the mixture \((\eta)^{20}\) rises until