



Soviet-era science, translated into English

Chemistry

Academician B. A. ARBUZOV and A. V. FUZHENKOVA

1957-01-01T00:00:00+00:00

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Abstract

Full Text

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STUDY OF THE A. E. ARBUZOV REARRANGEMENT BY THE THERMOGRAPHIC METHOD

A. E. Arbuzov⁽¹⁾, who discovered the rearrangement of phosphorous esters into alkylphosphinic acid esters under the action of alkyl halides, believed that the rearrangement proceeds through the formation of an intermediate product of addition of the alkyl halide to trivalent phosphorus. For aromatic phosphites the formation of an intermediate product was proved by isolating them. For aliphatic phosphites, intermediate products cannot be isolated, evidently owing to their instability*.

In our communication⁽³⁾ we presented the results of a study of the interaction of phosphorous acid esters with alkyl halides by the method of physicochemical analysis—by constructing “composition—property” diagrams. In a number of cases the possibility was shown of using this method to prove the formation of an intermediate addition product in the course of the A. E. Arbuzov rearrangement.

In the present communication we give the results of studying the A. E. Arbuzov rearrangement by the thermographic method. The thermographic method makes it possible readily to detect the presence of processes accompanied by the evolution or absorption of heat. It might have been expected that the thermographic method would make it possible to detect the moment of formation of the intermediate product of addition to trialkyl phosphite and then the moment of its decomposition into an alkyl halide and an alkylphosphinic acid ester.

Fig. 1. Thermogram of a mixture of $(P(OC_6H_5)_3)$ and (CH_3J) . Heating rate—6–7 deg/min

To test the possibilities of the thermographic method, we recorded thermograms of the system triphenyl phosphite—methyl iodide, for which the addition product had been isolated in pure form⁽⁴⁾, and also of certain other halogen derivatives with triphenyl phosphite.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Indeed, in most of the systems investigated, two exothermic effects were found on the thermograms. In some cases, at high temperatures a third effect appears, which should be associated with decomposition of the reaction product under the action of high temperature.

Data for the system triphenyl phosphite–methyl iodide are given in

* In the literature there are statements concerning a mechanism of the A. E. Arbuzov rearrangement without participation of an intermediate product of the quasiphosponium type (2).

Fig. 1. On the thermogram the presence of two exothermic effects is clearly seen at temperatures of 227 and 370° at a heating rate of 6–7 deg/min.

That both of these effects are a reflection of two processes in the A. E. Arbuzov reaction is evidenced by thermograms recorded for the previously obtained product of the addition of methyl iodide to triphenyl phosphite. In the latter case the exothermic effect coincides with the second effect of the triphenyl phosphite–methyl iodide system at the same heating rate (3 deg/min). For the triphenyl phosphite–methyl iodide system the second exothermic effect is observed at 292°, while for the addition product the effect of its decomposition to phenyl methylphosphonic acid ester occurs at 293°.

Fig. 2. Thermograms of a mixture of $P(OC_6H_5)_3$ and C_2H_5I . *a* –heating rate, 5 deg/min; *b* –heating rate, 0.4 deg/min

The equimolecular mixture of triphenyl phosphite and methyl iodide, at the moment of the maximum of the first effect (197°), was removed from the furnace and cooled. The contents of the small vessel crystallized into a solid mass of crystals of the product of addition of methyl iodide to triphenyl phosphite. Upon repeated heating of this small vessel, only the second exothermic effect was obtained, at 305°.

An analogous picture was also obtained in the case of the triphenyl phosphite–benzyl iodide system.

Fig. 3. Thermogram of a mixture of $P(OC_2H_5)_3$ and $C_6H_5CH_2I$. Heating rate, 4–5 deg/min

Two exothermic effects were obtained on thermograms for systems of triphenyl phosphite and, respectively, methyl bromide, ethyl bromide, and propyl bromide,

Fig. 4. Thermogram of a mixture of (P(OC_2H_5)_3) and (CH_2BrC HBrOC_2H_5).

Figure 4: Fig. 4. Thermogram of a mixture of (P(OC_2H_5)_3) and (CH_2BrC HBrOC_2H_5).

α,β -dichlorodiethyl ether and α,β -dibromodiethyl ether.

The thermographic study of the interaction of aliphatic phosphites with halogen derivatives was carried out by us using trimethyl phosphite and triethyl phosphite with the following halogen derivatives as examples: CH₃I, C₂H₅I, iso-C₃H₇I, iso-C₄H₉I and *n*-C₄H₉I, C₆H₅CH₂I, CH₃Br, C₂H₅Br, *n*-C₃H₇Br, *n*-C₄H₉Br, and C₆H₅CH₂Br.

These examples show that the interaction of the listed halogen derivatives with trimethyl phosphite and triethyl phosphite at a heating rate of 4-5 deg/min is, as a rule, accompanied by only one exothermic effect. As an example we cite the triethyl phosphite–ethyl iodide system (Fig. 2, *a*).

With an increase in the molecular weight of the alkyl halide, the temperature at which the components interact increases. The temperature at which interaction begins for alkyl halides of iso-structure is higher than for alkyl halides of normal structure.

For the systems triethyl phosphite–methyl bromide and triethyl phosphite–benzyl iodide, two exothermic effects were obtained on the thermograms: for benzyl iodide at 97-99 and 150-152° (Fig. 3). On repeating the experiments, the thermograms were well reproduced. Evidently, the first effect corresponds to the formation of the addition product of benzyl iodide to triethyl phosphite, and the second to the decomposition of the intermediate product into ethyl iodide and the ethyl ester of benzylphosphinic acid.

With benzyl bromide and benzyl chloride and triethyl phosphite, under the same heating conditions, only one exothermic effect is observed.

The presence in a number of examples of a single exothermic effect may be explained by the fact that, at the heating rates used (4-5 deg/min), the reaction proceeds so rapidly that on the thermograms the two stages are not recorded separately, but merge into one exothermic effect.

In such a case, with slower heating one could expect the appearance of two exothermic effects.

Indeed, experiment showed that at heating rates of 0.4 deg/min (instead of 4 deg/min, when the reaction is completed not in 60 min, but in 11 h), on the thermogram of the triethyl phosphite–ethyl iodide system two exothermic effects are indicated (see Fig. 2, *b*).

Fig. 4. Thermogram of a mixture of (P(OC_2H_5)_3) and (CH_2BrC HBrOC_2H_5).

If triethyl phosphite with benzyl bromide, on rapid heating, gave only one effect, then at a heating rate of 0.4 deg/min two exothermic effects are clearly expressed on the thermogram (73 and 160°).

Interesting results were obtained for the systems triethyl phosphite– α,β -dichloroethyl ether and triethyl phosphite– α,β -dibromoethyl ether.

V. S. Abramov and G. Karp (5) showed that α,β -dibromoethyl ether reacts with phosphites even at -3° with evolution of heat. At the same time the odor and lacrimatory action of the dibromoethyl ether disappear; a small change occurs in the specific gravity and refractive index, which, in the opinion of V. S. Abramov and G. Karp, indicates the formation of an intermediate product of the quasiphosphonium type.

The thermogram of an equimolecular mixture of triethyl phosphite and α,β -dichloroethyl ether at a heating rate of 5 deg/min shows two exothermic effects at 155 and 200–212°. For α,β -dibromoethyl ether and triethyl phosphite, interaction occurs at 25°. At this temperature an intermediate compound is formed. Its decomposition begins at a temperature of 117–125° (Fig. 4). The following fact indicates that at this temperature it is precisely the intermediate addition product that decomposes. An equimolecular mixture of triethyl phosphite and α,β -dibromoethyl ether, after mixing, was kept at room temperature for 6 days, after which it was heated thermographically. On the thermogram only one exothermic effect is indicated, which coincides with the second exothermic effect of the thermogram taken immediately after mixing the components.

Thus, the thermographic method indicates the formation of interme-

of the final product in the A. E. Arbuzov rearrangement not only for aromatic phosphites, but also for aliphatic esters of phosphorous acid.

In the case of aliphatic esters of phosphorous acid, the intermediate products are very unstable and readily decompose into an alkyl halide and an ester of alkylphosphinic acid.

Kazan State University
named after V. I. Ulyanov-Lenin

Received
18 XII 1956

CITED LITERATURE

- ¹ A. E. Arbuzov, *On the structure of phosphorous acid and its derivatives*, Dissertation, 1905. ² R. Rumpf, Bull. Soc. Chim., No. 3–4, p. 128 (1951). ³ B. A. Arbuzov, A. V. Fuzhenkova, DAN, 113, No. 6 (1957). ⁴ A. E. Arbuzov, N. P. Nesterov, DAN, 92, 57 (1953); Izv. AN SSSR, OKhN, 1954, 427. ⁵ V. S. Abramov, G. Krap, DAN, 91, 1095 (1953); ZhOKh, 24, 1823 (1954).

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