

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 Arbusov rearrangement.

#### SUMMARY

1. Raising the pressure from 2000 kg/cm<sup>2</sup> 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 Arbusov 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.

#### LITERATURE CITED

1. M. G. Gonikberg and I. Z. Fainshtein, Dokl. AN SSSR, 147, 612 (1962).
2. I. Z. Fainshtein and M. G. Gonikberg, Izv. AN SSSR, Ser. khim., 1401 (1964).
3. A. E. Arbusov, Dissertation [in Russian], St. Petersburg, (1905); Selected Works [in Russian], Izd. AN SSSR (1952), p. 111.
4. A. E. Arbusov and L. V. Nesterov, Izv. AN SSSR, Otd. Khim. N., 427 (1954).
5. L. V. Nesterov, Dissertation [in Russian], Kazan' (1953).
6. S. R. Landauer and H. N. Rydon, J. Chem. Soc. 2224 (1953).
7. C. Walling and J. Pellon, J. Amer. Chem. Soc. 79, 4776 (1957).
8. M. G. Evans and M. Polanyi, Trans. Faraday Soc. 31, 875 (1935).
9. T. I. Temnikova, Course in the Theoretical Bases of Organic Chemistry [in Russian]. Second Edition, Goshkimizdat, Leningrad (1962), p. 782.
10. M. G. Gonikberg, Chemical Equilibrium and Reaction Rate at High Pressures [in Russian]. Second Edition, Izd. AN SSSR, Moscow (1960), p. 145.

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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.

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