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1958

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

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REACTIONS OF METHYL RADICALS, OBTAINED BY THE POLANYI METHOD, WITH DEUTERIUM

(Presented by Academician N. N. Semenov on 26 VII 1957)

Recently a number of works have appeared in the literature devoted to the investigation of processes of thermal and photochemical decomposition of organic compounds which form, in the primary act of decomposition, the radical CH_3, in the presence of molecular deuterium (1–5).

These investigations are carried out chiefly in order to determine the rate constant of the elementary substitution reaction of the methyl radical:

$$CH_3 + D_2 = CH_3D + D.$$

In the works cited, no methane containing more than one deuterium atom was found. We note only that Nesbitt, Gordon, and Smith (5), who carried out photolysis of a mixture of acetone with deuterium in the presence of small amounts of mercury, found, along with CH_3D, insignificant amounts of CH_2D_2.

On the other hand, Mardaleishvili, Pariiskii, Poltorak, and Voevodskii (6) discovered large amounts of deeply deuterated methane in studying the interaction with deuterium of methyl radicals obtained in the reaction of H atoms, drawn from an electric discharge, with olefins. The authors believe that these data may be regarded as confirmation of the hypothesis they had advanced earlier (7) concerning the existence of exchange between the hydrogen of free radicals and molecular deuterium. These experiments were arranged so as to exclude the participation of D atoms in the reaction, since in a number of experiments molecular deuterium was admixed at that point of the jet where the interaction of H atoms with unsaturated compounds could be considered to have ended.

The appearance of poly-substituted methanes could not have been connected with the low pressures at which the experiments with the electric discharge were carried out, since it was shown that, in the photolysis of acetone and methyl iodide, a change in pressure from tens to several tenths of a millimeter of mercury did not lead to the appearance of deeply exchanged methanes*.

Fig. 1. Diagram of the apparatus.

Figure 1: Fig. 1. Diagram of the apparatus.

The explanation of the indicated contradiction may lie in the different ways of obtaining methyl radicals. Therefore we set ourselves the task of studying the reaction with D_2 of methyl radicals obtained by some other method.

We obtained methyl radicals by the Polanyi method (8) according to the reaction:

$$CH_3J + Na = CH_3 + NaJ.$$

The reaction was carried out in the presence of molecular deuterium, which was used as the carrier gas for Na vapors. The scheme of the apparatus is shown in Fig. 1. The reaction vessel, in which the jets of CH_3J and deuterium saturated with sodium vapor were combined, was a quartz cylinder connected through a nozzle with a boat containing sodium, and through—

through another nozzle into a flask containing CH_3I. The temperature of the boat with sodium during the experiments was maintained at 450°.

In those cases where it was desirable to exclude a volume reaction, the boat with sodium was not heated. The pressure of CH_3I in the reaction vessel was 0.5 mm Hg, the pressure of D_2 was 10 mm, and the stream rate was 8.5 cm^3/min. The reaction products, together with the unreacted CH_3I, passed through a coil cooled with liquid nitrogen, where methyl iodide, as well as ethane and other condensable reaction products, were frozen out.

Fig. 1. Diagram of the apparatus. 1, 2, 3—flasks with CH_3I, D_2, and H_2, respectively; 4—trap for capturing mercury vapor from the manometer, 5—valves, 6—finger with liquid CH_3I, 7—boat with Na, 8—reaction vessel, 9—nozzle, 10—membrane manometer, 11, 12—furnaces, 13—finger with activated carbon, 14—trap, 15—coil, 16—trap with activated carbon, 17—comb for taking samples for analysis, 18—trap, 19—connection to the pump, 20—thermal manometer, 21—connection to the mercury manometer, 22—capillary, 23—connection to the atmosphere

Methane and part of the deuterium were captured in a trap with activated carbon, located after the coil and also cooled with liquid nitrogen. After the experiment was completed, the deuterium was pumped out of this trap, and the methane was sent for analysis. Mass-spectrometric analysis made it possible to judge the content of the variously deuterated methanes. The absolute amount of methane was not determined in most experiments.

In a number of experiments the inner surface of the reaction vessel was coated with sodium, deposited on the surface in the form of drops or as a mirror. The

* These results were obtained by A. S. Chernysheva.

Fig. 2

Figure 2: Fig. 2

drops were obtained either by splashing pieces of sodium placed in the vessel by rapidly heating them, or by rapidly heating it in the boat while simultaneously passing a stream of deuterium. The mirror was obtained by gradually heating the sodium placed in the vessel to 300°.

The work used deuterium obtained electrolytically from D_2O and purified from impurities by diffusion through a palladium capillary. CH_3I was distilled in a rectification column (b.p. 41.5-42°, $n^{19} = 1.532$). The sodium used was chemically pure and was not subjected to additional purification.

The composition of the methanes obtained in a pure quartz vessel in the temperature range 20-480° was determined (Fig. 2). Under these conditions CH_4 and CH_3D are formed predominantly. The amount of polydeuterated methanes is small and only in a narrow temperature interval near 200° reaches 18-20%. The ratio CH_3D/CH_4 increases in the interval 20-100° from 0.6 to 2, and does not change with a further increase in temperature.

It was found that the deuterium content in the methanes formed changes substantially when metallic sodium is deposited from the stream onto the surface of the vessel. Further experiments showed that the relation of the percentage

the content of differently deuterated methanes with temperature depends on how the sodium was applied to the surface.

When the surface of the vessel is coated with a sodium mirror (Fig. 3, *I*), the percentage content of deeply deuterated methanes (CD_4, CD_3H, and CH_2D_2) at room temperature is 5-8 times greater than in a clean quartz vessel. With increasing temperature the percentage of deeply deuterated methanes decreases. It seems to us, however, that the decrease is not connected with a reduction in the rate of formation of CD_4 and other heavier methanes. A direct experiment measuring the total concentration of methanes showed that, when the temperature was raised to 70°, the yield of methanes in the presence of a mirror increased by approximately a factor of 10. The decrease in the percentage content of CD_4, CH_2D_2, and CD_3H may therefore be explained by the presence of a heterogeneous reaction on the sodium surface, leading mainly to the formation of CH_4 and CH_3D.

Fig. 2. Dependence of the percentage content of methanes obtained in a clean reaction vessel on temperature:
a–CH_4, b–CH_3D, v–CH_2D_2, g–CH_3D, d–CD_4

In the case of sodium droplets, the surface reaction is insignificant, and its share of the volume formation of methane amounts to only 1/5. In this case the methanes obtained from CH_3 radicals formed in the gas phase contain much more deuterium than in the case of a sodium mirror (Fig. 3, *II*). A maximum of

Fig. 3

Figure 3: Fig. 3

deuteration near 70–80° is noteworthy. At higher temperatures CH_4 and CH_3D again predominate.

Fig. 3. Dependence of the percentage content of methanes obtained in a vessel coated with a Na mirror (*I*) and with drops of Na (*II*) on temperature. The designations are the same as in Fig. 2.

It is important to note that light methane CH_4 does not exchange with D_2 either in the presence of a mirror or in the presence of sodium droplets.

From these data, and also from the fact that the content of CD_3H is always less than that of CD_4 and CD_2H_2, it follows that, in our experiments, deeply exchanged methanes could not have appeared as a result of the successive replacement of H atoms by D in saturated methanes. Consequently, by whatever mechanism the formation of CH_2D_2, CH_3D, and CD_4 proceeded, this exchange must have taken place with the participation of methyl radicals.

The distribution of deuterated methanes in our experiments differs from the distribution in the experiments of Mardaleishvili, Pariiskii, Voevodskii, and Poltorak ([6]), which apparently indicates a different mechanism of their formation.

The role of the Na surface in the exchange of CH_3 radicals with deuterium in our case is undoubted; however, at present there are insufficient data for constructing a detailed mechanism that would explain the character of deuteration of the methanes, as well as the maximum at a temperature of 70–80°.

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Received
19 VII 1957

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