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Abstract

Full Text

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On the Question of Isotopic Exchange of Free Radicals with Deuterium

(Presented by Academician N. N. Semenov on 26 V 1962)

In the interaction of deuterium atoms with various organic compounds, deeply deuterated molecules of the final products are formed. Thus, methane formed in the reaction of D atoms with $CH_3{-}CO{-}CH_3$, $CH_3{-}O{-}CH_3$, and saturated and unsaturated hydrocarbons consists mainly of polysubstituted molecules CD_4, CD_3H, etc., with an average deuterium content of up to 98% ($^{1-3}$).

It is generally known that such deep deuteration of the products of these reactions is due to isotopic exchange of the free radicals formed in the process with deuterium atoms (^{4,1}).

$$\dot{C}H_3 + D \rightarrow \dot{C}H_2D + H \tag{A}$$

and so on up to $\dot{C}D_3$.

However, a quantitative analysis of the experimental data for these reactions led Voevodskii to the conclusion that the amounts of D atoms calculated on the basis of the degree of deuteration of the final products are, in some cases, 5-10 times greater than the amounts introduced into the system.

Since under the conditions of the experiments indicated molecular deuterium was always present in the system, Voevodskii, in order to explain the excess balance of D atoms, suggested that D_2 molecules may take part in the exchange with radicals according to the reaction:

$$\dot{C}H_3 + D_2 \rightarrow \begin{matrix} H_2C \cdots D \\ \dot{H} \cdots \dot{D} \end{matrix} \rightarrow \dot{C}H_2D + HD \tag{B}$$

and so on up to $\dot{C}D_3$.

To test this hypothesis, with the participation of one of us, experiments were carried out in which a mixture of ethylene and deuterium was added to a jet of partially dissociated hydrogen (protium). On the basis of reliable literature data it is known that the rate constants of reactions (1) and (2)

$$H + D_2 \rightarrow HD + D \tag{1}$$

$$H + C_2H_4 \rightarrow \dot{C}_2H_5 \qquad (2)$$

are respectively $1.4 \cdot 10^{-16}$ (^{5,6}) and $9 \cdot 10^{-13}$ cm^3/sec (^{7}). These values of the constants give grounds to believe that, in Voevodskii' s experiments, the ratio of the rates of reactions (1) and (2) is 10^{-3}, i.e., protium atoms are consumed mainly in the formation of radicals by reaction (2), while the appearance of D atoms by reaction (1) in the system practically does not occur. Therefore, in these experiments,

carried out in the absence of D atoms, it was expected that the presence or absence of deep exchange in the reaction products would make it possible to decide the question, respectively, in favor of or against the postulated mechanism of exchange of radicals with molecular deuterium.

As a result of studying the reaction of partially dissociated protium ($H + H_2$) with various olefins in the presence of molecular deuterium, it was established that the reaction products formed under these experimental conditions were deuterated to a considerable extent and, in particular, up to the equilibrium exchange of the corresponding radicals with the mixture $H_2 + D_2$. Even in the case in which the radicals were generated by means of deuterium atoms, for example in the system $(D + D_2) + (C_2H_4 + H_2)$, the extent of exchange of the products remained dependent only on the isotope composition of hydrogen $(H_2 + D_2)$ (^{8,9}).

It seemed that the results of the experiments carried out could serve as unambiguous proof of the participation of molecular deuterium in exchange with free radicals according to a reaction of type (B). However, in a number of subsequent experiments carried out in the absence of D atoms, in particular in the study of the photolysis of acetone in the presence of molecular deuterium ($^{10-12}$), and also in our work on the thermal decomposition of certain ketones in the presence of D_2 (^{13}), no formation of polydeuterated molecules of the final products was detected, which should have occurred if the process of exchange of radicals with molecular deuterium were real.

In view of the contradiction that appeared between the results of the two series of studies, we carried out additional experiments on measuring the rates of reactions (1) and (2) under the conditions of the experiments of Voevodskii et al. (^{8,9,2}), by determining the rate of formation of HD (and, consequently, of D or H atoms, respectively) in the systems $(H + H_2) + (C_2H_4 + D_2)$ and $(D + D_2) + (C_2H_4 + H_2)$ at various concentrations of the reacting components.

As a result of this series of experiments it was established that, along with the homogeneous reaction (1), which proceeds at an extremely low rate in comparison with the rate of reaction (2), under the conditions of the experiments of Voevodskii et al. a considerably faster heterogeneous-catalytic reaction ($1'$) is observed on the wall of the reaction vessel (glass, quartz):

$$H + D_2 \xrightarrow{\text{wall}} HD + D. \tag{1'}$$

This circumstance leads to the replacement of H atoms by D atoms in the system, which also accounts for the appearance in the products of deuterium atoms in the above-mentioned amount, exceeding that calculated by taking into account only reactions (1) and (2)*. The results of the study of the heterogeneous-catalytic effect in the reaction of exchange of atoms and molecules of hydrogen (protium, deuterium) are of independent interest and will be presented in our subsequent paper.

In the present communication we wish only to note that the so-called phenomenon of exchange of free radicals with molecular deuterium does not occur. The erroneous conclusion as to its reality is based on an insufficiently rigorous interpretation of the experimental data, which did not take into account the then still unknown heterogeneous-catalytic reaction (1′), leading to the appearance in the system of additional amounts of deuterium atoms relative to those introduced into the system. We considered it necessary to illuminate this question in some detail, since the erroneous conclusion about the mechanism of molecular exchange has become widespread ([14–16]).

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* In contrast to the experiments in which the aforementioned ratio of the rate constants of reactions (1) and (2) was measured, under the conditions of the experiments of Voevodskii et al. the reaction was carried out by the Bonhoeffer-Wood method in a stream of reacting gases at low pressures (< 0.1 mm Hg), in consequence of which, owing to facilitated diffusion, the fraction of processes occurring on the reactor wall increases.

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