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Abstract

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THE INFLUENCE OF THE PHASE STATE ON THE CHARACTER OF THE REACTIONS OF TRITIUM RECOIL ATOMS IN MIXTURES OF CYCLOHEXANE WITH BENZENE

(Presented by Academician V. I. Spitsyn on 1 VII 1963)

The study of the processes of slowing down and stabilization of tritium recoil atoms in hydrocarbons has shown that the most probable products of "hot" reactions, proceeding through the stage of formation of an excited complex or an excited molecule, are HT and the labeled parent compound (ˆ1). At the same time, the probability of retention of a recoil atom in the molecule of an organic compound is to a large extent determined by the effectiveness of intramolecular and intermolecular energy scattering. Consequently, an increase in the concentration in a binary mixture of a component that is an excitation acceptor, or the strengthening of intermolecular interaction on going from the gaseous state to the liquid and then to the solid, should promote an increase in the specific activity of the irradiated compound. Recently several papers have been published confirming this point of view (2-6).

In the present work, the influence of the phase state on the probability of hydrogen-abstraction and hydrogen-substitution reactions by tritium recoil atoms in mixtures of benzene with cyclohexane was studied.

Mixtures of 0.02 g of lithium carbonate and 0.015 g of organic substance were irradiated in quartz ampoules of volume 0.3 cm^3 for 20 min with a flux of $2 \cdot 10^{12}$ n/cm^2 sec at 40 and $-195°$. For irradiation in the gas phase, 0.008 g of organic substance was placed in quartz ampoules of volume 3.5 cm^3, on the walls of which a layer of lithium carbonate, taken in an amount of 0.5 g, had previously been deposited in the molten state. In this case the samples were irradiated for 2 hours with a flux of $1 \cdot 10^{12}$ n/cm^2 sec at 150°. The vapor pressure in the ampoules during irradiation was about 1 atm. The samples were analyzed by a gas-chromatographic method, as described previously (ˆ2).

Owing to the small range of tritium recoil atoms, a certain fraction of them is stopped in the crystals of the lithium salt. Therefore, depending on the size

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of the crystals, the geometrical conditions, and also on the relative amounts of organic substance and lithium carbonate, the fraction of recoil atoms entering into "hot" reactions may vary greatly. At the same time, the ratio of the yields of different tritium-labeled products remains constant and does not depend on the magnitude of the total recorded activity. Tritium atoms absorbed in the particles of the lithium salt are retained very firmly in it and do not participate in reactions leading to the formation of liquid and gaseous labeled products. Thus, practically all the activity recorded in the gas and liquid fractions of the samples represents the product of the interaction of "hot" tritium atoms with organic compounds, while the distribution of activity among the individual labeled components characterizes the probability of the different pathways for stabilization of recoil atoms. The average values of the total activities do not differ appreciably for the hydrocarbons studied and their mixtures. The data obtained are presented in Fig. 1 in the form of the ratio of the activities of the individual products to the total activity of the gas and liquid fractions of the sample, taken as 100.

It follows from the data obtained that, when the aggregate state changes, the distribution of activity between the gas and liquid fractions for the individual hydrocarbons and their mixtures does not remain constant. In all cases, a clearly expressed tendency toward a decrease in the yield

HT and to an increase in the activity of hydrocarbons upon transition from the gas to the condensed phases. The increased possibility of retaining the "hot"atom in the organic molecule, undoubtedly caused by a corresponding decrease in the probability of hydrogen abstraction as the intermolecular interaction becomes stronger, confirms that the direction of decomposition of the excited complex (excited molecule) is largely determined by the properties of the surrounding medium.

Retention in the benzene molecule in any aggregate state is significantly higher than in HT; for cyclohexane the opposite phenomenon occurs.

Fig. 1. Distribution of activity between the gas fraction and the components of binary mixtures of benzene with cyclohexane. 1 –HT, 2 –C_6H_6, 3 –C_6H_{12} (solid phase); 1′ –HT, 2′ –C_6H_6, 3′ –C_6H_{12} (liquid phase); 1″ –HT, 2″ –C_6H_6, 3″ –C_6H_{12} (gas phase)

The change in the probability of labeling a benzene molecule with tritium upon transition from the solid phase to the liquid is somewhat smaller than from the liquid to the gas. In the case of cyclohexane, retention in the parent molecule for the solid phase is slightly greater than for the liquid and decreases more strongly upon transition to the gaseous state than in the case of benzene.

The distribution of activity between the components of binary mixtures and the gas fraction in all aggregate states qualitatively coincides with the picture obtained by us earlier for the liquid phase: the activity of the gas fraction changes almost linearly between the values corresponding to the individual hydrocarbons; the radiochemical yields of the mixture components are not a linear function of concentration, and for benzene they are always smaller, while for cyclohexane they are larger, than would be expected from the properties of the individual hydrocarbons. The specific activities of the mixture components, calculated as the ratios of radiochemical yields to mole fractions, in all cases increase linearly with increasing mole fraction of benzene, from which it follows that the phenomena of "protection" and "self-protection" occur in all aggregate states.

The relative effectiveness of the "self-protection" of benzene increases noticeably upon transition from the liquid state to the solid. When its mole fraction in the mixture with cyclohexane is changed from 1.0 to 0.1, the specific activity of benzene falls in the solid phase by 35%, in the liquid by a factor of 1.7, and in the gas by approximately a factor of three. For cyclohexane no such clear dependence is observed.

Owing to the fact that the specific activity of benzene decreases with decreasing concentration in the mixture more rapidly than the specific activity of cyclohexane, these quantities approach each other in a medium rich in cyclohexane. This effect increases regularly upon transition from the solid phase to the liquid and gas phases; in the latter case the specific activity of benzene almost does not exceed the specific activity of cyclohexane. It follows from this that the probability of labeling an individual isolated benzene molecule at infinite dilution in cyclohexane vapor practically does not differ from the probability of labeling cyclohexane itself, and, consequently, the sharp increase in the specific activity of benzene with its concentration in the mixture and upon transition from the gas to the condensed phases is due exclusively to an increase in the efficiency of energy transfer from the excited intermediate product to the surrounding medium.

On the basis of a study of the X-ray spectra of benzene and cyclohexane (7), conclusions were drawn concerning the existence in liquid hydrocarbons of a considerable number of associated regions, i.e., short-lived groupings of molecules oriented as in a crystal lattice. In binary mixtures the degree of ordering of both components decreases appreciably; however, the presence of associated groups of molecules of one type has also been observed in highly dilute solutions. It is therefore natural that the transition from the gaseous state, where all molecules are completely isolated, to the liquid state affects both hydrocarbons more strongly than the transition from an already substantially organized liquid phase to the solid phase.

The sharp increase in the specific activity of benzene on going to states with a more ordered structure makes it possible to assume that "self-protection" is effected most efficiently by ensembles of organized benzene molecules, whereas for cyclohexane the protective role of benzene apparently does not increase with increasing degree of its organization.

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