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schematic transition states labeled (A) and (B)

Figure 1: schematic transition states labeled (A) and (B)

Abstract

Full Text

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ISOMERIZATION OF THE *n*-PROPYL RADICAL

The possibility of isomerization of free radicals in the liquid phase by hydrogen migration has been investigated in a number of works ([1]-[3]); however, until recently the only reliable indication of the occurrence of such a rearrangement was the report by Grob and Camenisch ([4]), who observed isomerization of the 5-phenylamyl radical during thermolysis of ϵ-phenylcaproic acid peroxide. With respect to the ability to undergo rearrangement, in particular by hydrogen transfer, the behavior of radicals in solution differs sharply from that of carbonium ions, for which such rearrangements are well known; this points to a considerably larger value of the ratio $K_{\text{subst}}/K_{\text{isomer}}$ in the case of radicals. In view of the small content of the isomerized compound in the reaction products, the latter can be detected only by the most sensitive methods.

Using radiocarbon, one of us and T. N. Shatkina showed ([5]) that the radical CH_3—CH_2—$C^{14}H_2$·, formed upon decomposition in carbon tetrachloride at 76° of butyryl peroxide labeled in the α-position, undergoes, by hydrogen migration from the β-position, isomerization into the radical $C^{14}H_3$—CH_2—CH_2·.

The percentage of isomerization was $3.9 \pm 0.5\%$. Apparently, the symmetry of the transition state (A) during migration is of considerable importance for the occurrence of hydrogen migration; in the case of the propyl radical this symmetry is maximal, as compared with the transition state (B) in the case of other alkyl radicals.

(A) (B)

It is possible that it is precisely the asymmetry of the transition state in the case of the *n*-hexyl radical that accounts for the absence of isomerization found by De Tar ([6]) during decomposition of heptanoyl peroxide*.

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* It is also possible that in radicals of the type R—CH_2—CH_2—CH_2· a factor hindering rearrangement is the relatively greater (in comparison with

conformation diagram labeled (B)

Figure 2: conformation diagram labeled (B)

CH_3—CH_2—CH_2·) conformational weight of the type (B), which is due to repulsion between the groups R— and —CH_2·. This conformation is unfavorable for formation of the four-membered transition state (B), in which three carbon atoms and a hydrogen atom must lie in one plane.

(B)

In order to obtain additional information on the nature of the rearrangement of the propyl radical and on the influence of various factors on it (the structure of the radical, the nature of the medium, temperature, etc.), we studied the behavior of *n*-propyl-1-H_2^2 and *n*-propyl-1-H_1^3 radicals during the decomposition of butyryl peroxides labeled in the τ-position, respectively with deuterium and tritium, in carbon tetrachloride and bromoform at various temperatures.

The introduction of a hydrogen isotope into the radical, besides making it possible to obtain independent confirmation of the very fact of isomerization, made it possible to study the influence of the smallest possible structural changes on the occurrence of hydrogen migration. Namely, it could be expected that the presence of a hydrogen isotope (two deuterium atoms or one tritium atom) in position I of the radical would lead to a lowering of the degree of isomerization owing to a decrease in the symmetry of the transition state.

The experimental data obtained are in agreement with such an assumption: the isomerization amounts to $1.3 \pm 0.1\%$ in the case of the I-H_2^2 radical and $0.6 \pm 0.07\%$ in the case of the I-H_1^3 radical. The peroxide decomposition was carried out under the standard conditions described earlier ([5]) (in CCl_4 at $t = 76^\circ$). The method used to establish the position of the label was analogous to that used earlier ([5]) in the case of the study with radiocarbon. For example, for the case of tritium, the scheme for establishing the position of the label is as follows:

$$\begin{cases} CH_3CH_2CHTCl \\ CH_2TCH_2CH_2Cl \end{cases} \xrightarrow{K_2CO_3} \begin{cases} CH_3CH_2CHTOH \\ CH_2TCH_2CH_2OH \end{cases} \xrightarrow{KMnO_4} \begin{cases} CH_3CH_2COOH \\ CH_2TCH_2COOH \end{cases}$$

It was additionally verified that there was no hydrogen exchange and no side reactions involving redistribution of the label at the stages of hydrolysis of propyl chloride and oxidation of the resulting *n*-propyl alcohol to propionic acid.

The percentage of isomerization was found as the ratio of the deutero-tritium content of the propionic acid to the deutero-(tritium)-content of the starting butyric acid. Analysis for deuterium content was carried out by combustion to water with subsequent determination of the heaviness by the drop method

([7]); to determine the tritium content, the substances were oxidized to water, which was then reduced to hydrogen by Simon' s method ([8]); the activity of the hydrogen was measured with the aid of an internal-filling counter.

We also investigated the influence exerted on the rearrangement of the *n*-propyl-1-H_2^2 radical by replacing the solvent—carbon tetrachloride—with bromoform. The choice of bromoform as solvent was due to the fact that the energy of the C—Br bond is considerably less* than the energy of the CCl bond (in CCl_4), and, consequently, the ratio $K_{\text{subst}}/K_{\text{isomer}}$ should be greater in the first case, which in turn should lead to a decrease in the percentage of isomerization. Experimentally it was found that the degree of isomerization was 0.51%, i.e., 2.5 times less than in the case of CCl_4.

Next, the influence of temperature on the degree of isomerization during the decomposition of α,α-di-deuterobutyryl peroxide in bromoform was studied. On the basis of theoretical considerations, it appears probable that the ratio $K_{\text{subst}}/K_{\text{isomer}}$ will decrease with increasing temperature (N. N. Semenov ([9])).

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* Free alkyl radicals in reaction with $CHCl_3$ abstract hydrogen, and in reaction with $CHBr_3$, a bromine atom.

However, within the experimental error, we obtained identical results at two different temperatures (0.5$±0.25±$0.25% at 140°). Further study of the radical isomerization reaction over a broader temperature range is necessary.

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Note: Figure translations are in progress. See original paper for figures.