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Corresponding Member of the Academy of Sciences of the USSR O. A. REUTOV and T. N. SHATKINA

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Abstract

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ISOMERIZATION OF THE FREE *n*-PROPYL RADICAL IN SOLUTION

In 1941 Kharasch et al. (1), decomposing *n*-butyryl peroxide and *iso*-butyryl peroxide in carbon tetrachloride, found that in the first case only *n*-propyl chloride is formed, and in the second—exclusively isopropyl chloride. On the basis of these results, Kharasch concluded that free alkyl radicals are incapable of isomerization.

Using the carbon isotope C^{14}, we found that the free propyl radical formed during the thermal decomposition of *n*-butyryl peroxide in solutions according to the reaction

$$(CH_3CH_2CH_2COO)_2 \rightarrow 2CH_3 - CH_2 - CH_2 \cdot + 2CO_2,$$

undergoes isomerization of the following type:

$$CH_3 - CH_2 - C^{14}H_2 \cdot \rightleftarrows \cdot CH_2 - CH_2 - C^{14}H_3.$$

The decomposition of *n*-butyryl peroxide labeled in the α-position was carried out in boiling carbon tetrachloride

$$(CH_3 - CH_2 - C^{14}H_2 - COO)_2 + 2CCl_4 \rightarrow 2CH_3 - CH_2 - CH_2 - Cl + 2CO_2 + CCl_3 - CCl_3.$$

To determine the position of the C^{14} atom in the molecule of propyl chloride, the latter was hydrolyzed to *n*-propyl alcohol; the alcohol was oxidized to propionic acid, and the propionic acid was oxidized to acetic acid.*

$$CH_3 - CH_2 - CH_2 - Cl \xrightarrow[(K_2CO_3)]{H_2O} CH_3 - CH_2 - CH_2 - OH \xrightarrow{KMnO_4}$$

$$\rightarrow \ CH_3 - CH_2 - C(=O)OH \xrightarrow{K_2Cr_2O_7} CH_3 - C(=O)OH$$

The acetic acid proved to be active (about 4% of the initial activity of the peroxide). From this fact it follows that a portion of the *n*-propyl radicals underwent rearrangement.

To establish the position of carbon C^{14} in the acetic acid molecule, we, on the one hand, fused its sodium salt with alkali and, on the other hand, carried out Schmidt degradation:

$$\text{a)}\quad CH_3 - COONa + NaOH \rightarrow C^{14}H_4 + Na_2CO_3,$$

$$\text{b)}\quad CH_3 - COOH + HN_3 \rightarrow C^{14}H_3 - NH_2 + CO_2 + N_2.$$

In the first case we found that the soda formed was inactive. In the second case it was found that all the activity from the acetic acid had passed into methylamine.

From the activity values of acetic acid and methylamine obtained by us in three parallel experiments, it follows that the isomerization of the *n*-propyl radical under the indicated conditions proceeds to an extent of $4.0 \pm 0.5\%$.

* Special experiments established that no rearrangement occurs at the stage of hydrolysis of propyl chloride.

Thus, the *n*-propyl radical in solution isomerizes with migration of a hydrogen atom from the *β*-position*, and not with migration of a methyl group,

$$CH_3—CH_2—C^{14}H_2 \rightleftharpoons \cdot CH_2—C^{14}H_2—CH_3,$$

as we initially believed ([3]), on the basis of analogy with the results on the isomerization of the propyl cation obtained by Roberts and Halmann ([4]).

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* V. V. Voevodskii and R. E. Mardaleishvili ([2]), studying the exchange of free alkyl radicals with deuterium, were the first to show the possibility of radical isomerization in the gas phase as a result of migration of hydrogen atoms from the β-position. The absence of isomerization of alkyl radicals in solution through migration of hydrogen atoms from the α-position follows from the above-cited work of Kharasch ([1]).

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