Chemistry

1965

SovietRxiv

Abstract

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Chemistry

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On the Sequence of Autoxidative Transformations of Normal Alkanes

(Presented by Academician B. A. Kazanskii, 3 VII 1964)

According to current concepts ($^{1-3}$), the stable products of the oxidation of hydrocarbons by molecular oxygen (alcohols, carbonyl compounds, acids, esters) are formed in the course of the oxidative process as a result of further transformations of intermediately arising peroxide compounds, which, in the case of oxidation in the liquid phase, are predominantly hydroperoxides of hydrocarbons (^{4,5}).

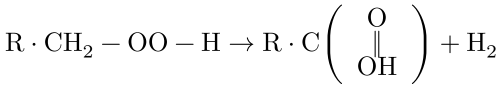
These views found expression in the scheme of V. Langenbeck and V. Pritzkow, proposed by them in 1950 (^{6})

Scheme I

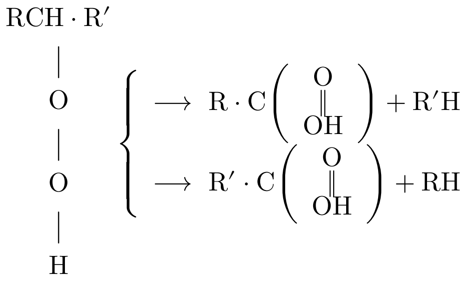
$$\begin{tikzcd}
 & \text{alcohol} & \\
\text{Hydrocarbon} \arrow[r] & \text{hydroperoxide} \arrow[u] \arrow[r] \arrow[d] & \text{ketone} \\
 & \text{[ketone hydroperoxide]} \arrow[r] & \text{acid [+aldehyde]}
\end{tikzcd}$$

and used later by many other investigators as applied to processes of slow oxidation of paraffin hydrocarbons in the liquid phase.

However, new experimental data on the decomposition of hydroperoxides of normal alkanes under various conditions show that these reactions are more complex than had been assumed until now, that they proceed simultaneously in several directions and that, therefore, the sequence of formation of molecular products of hydroperoxide decomposition given in the Langenbeck-Pritzkow scheme requires refinement and supplementation. Indeed, in addition to decomposition leading to the appearance of alcohols and carbonyl compounds and, as a result of subsequent oxidation of the latter, to acids, alkyl hydroperoxides at moderate temperatures undergo direct decomposition to a carboxylic acid and hydrogen (primary hydroperoxides) or to a hydrocarbon (secondary hydroperoxides), according to the reactions:



$$R\cdot CH_2-OO-H\rightarrow R\cdot C\left(\begin{matrix}O\\ \|\\ OH\end{matrix}\right)+H_2 \tag{1}$$

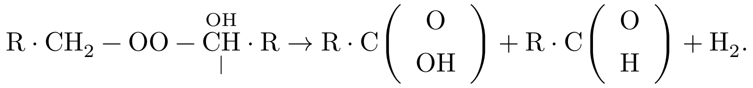


$$\begin{matrix}RCH\cdot R'\\ |\\ O\\ |\\ O\\ |\\ H\end{matrix}\left\{\begin{matrix}\longrightarrow R\cdot C\left(\begin{matrix}O\\ \|\\ OH\end{matrix}\right)+R'H\\ \longrightarrow R'\cdot C\left(\begin{matrix}O\\ \|\\ OH\end{matrix}\right)+RH\end{matrix}\right. \tag{2}$$

This was shown for the example of the primary hydroperoxide of *n*-butyl, which in pure form (in the absence of solvent) decomposes in an atmosphere of N_2 at 86–100° by 45–50% according to reaction (1) (^{7}), and upon decomposition of per-

primary hydroperoxide of *n*-amyl in an inert solvent (chlorobenzene), also in the absence of oxygen, at 110°, as a result of which, per mole of decomposed hydroperoxide, more than 0.4 mole of valeric acid and more than 0.2 mole of hydrogen were obtained (^{8}). Decomposition of primary amyl hydroperoxide in an oxygen atmosphere under the same conditions gave an even higher yield of these products. On decomposition of secondary amyl hydroperoxide (pentane hydroperoxide-2) in chlorobenzene solution in an atmosphere of N_2 at 110°, 0.05 mole of butyric acid and 0.04 mole of methane were obtained (in an O_2 atmosphere, somewhat less) (^{8}). From this it may be concluded that, in contrast to earlier ideas, the principal direction of decomposition of primary alkyl hydroperoxides in the liquid phase in an atmosphere of N_2 and O_2 is cleavage according to reaction (1) to hydrogen and an acid with the same number of C atoms in the molecule, whereas secondary alkyl hydroperoxides, in addition to the main direction of cleavage to a ketone (and water) and an alcohol with the same carbon skeleton, are capable of decomposing according to reaction (2) to acids with a smaller number of C atoms and hydrocarbons.

A more detailed study of the mechanism of reaction (1) (^{9}) made it possible to suggest that, in the case of decomposition of a primary hydroperoxide, an alkyl-1-hydroxy peroxide may first be formed as an intermediate product (as a result of condensation of the aldehyde, arising at first, with the same number of C atoms as in the initial peroxide compound, with a new molecule of hydroperoxide), which then decomposes mainly to an acid, hydrogen, and an aldehyde:



$$R\cdot CH_2-OO-\overset{OH}{\underset{|}{CH}}\cdot R\rightarrow R\cdot C\left(\begin{matrix}O\\ OH\end{matrix}\right)+R\cdot C\left(\begin{matrix}O\\ H\end{matrix}\right)+H_2. \tag{3}$$

Taking these data into account, and also taking into consideration recent experimental studies which have shown that alcohols in the zone of liquid-phase oxidation of hydrocarbons can readily be further oxidized to carbonyl compounds (with simultaneous formation of H_2O_2) ($^{10-12}$), the scheme of thermal decomposition of primary alkyl hydroperoxides in the presence of O_2 may be represented as follows:

Scheme II

```
                         \rightarrow Alcohol \rightarrow Complex ester \rightarrow Further
                         |              products
                         | +O_{2} \rightarrow H_{2}O_{2}
                         ↓
Primary hydroperoxide \rightarrow Aldehyde +O_{2} \rightarrow Acid \rightarrow Further
              |   H_{2}O                            products
              ↓
          Hydroxy peroxide          \rightarrow H_{2}
                         ↑                  ↑
```

In this and the following schemes, the sequence of formation is shown of molecular, relatively stable products in the initial stage of shallow decomposition of monohydroperoxides at moderate temperatures. In doing so, however, it must be borne in mind that under more severe conditions and under the influence of radicals formed as intermediates by the decomposing hydroperoxide, acids and esters that are stable under ordinary conditions may undergo further transformations (coupled decarboxylation (^{13}) and coupled oxidation of acids (^{10,20,22}), etc.); the initial monohydroperoxides themselves may also be oxidized with the formation of peroxide compounds containing several $-OO-H$ groups in the molecule (polyatomic hydroperoxides) (^{23}).

There are statements in the literature that ketones, unlike aldehydes, do not react with alkyl hydroperoxides with formation of hydroxy peroxides (^{14}), which was confirmed in our control experiments with pentanone-2 and secondary amyl hydroperoxide (pentane hydroper-

kis-2). Thus, for the case of decomposition of secondary alkyl hydroperoxides by reaction (2), the assumption of the possible intermediate formation of hydroxyperoxides is no longer applicable, and the scheme of their decomposition at moderate temperature in the presence of oxygen is represented as follows:

Scheme III

```
                          \rightarrow Alcohol \rightarrow Esters   \rightarrow Further prod
                                       ↑
                            +O_{2} \rightarrow H_{2}O_{2}
Secondary hydroperoxide   \rightarrow Ketone +O_{2} \rightarrow Acids \rightarrow Further pr

                                ↓
                              H_{2}O
```

```
                                        \rightarrow RH
                                        ↑
```

At present it may be considered established that the attack of molecular oxygen in the noncatalytic oxidation of paraffin hydrocarbons of normal structure in the liquid phase is directed mainly at the methylene groups of the carbon chain ($^{15-19,10}$) (with a probable preference for C_2-atoms (^{15,21,22})) and only to a small extent at the terminal methyl groups. That the latter nevertheless occurs is confirmed by the finding, in the products of liquid-phase oxidation of individual paraffins, of acids and primary alcohols with the same number of C-atoms as in the starting hydrocarbon (^{10,12,18,22}).

Thus, in the oxidation in the liquid phase of a normal paraffinic hydrocarbon, there must arise as initial intermediate products, in addition to the main mass of secondary hydroperoxides, a small amount of primary alkyl hydroperoxide (hydroperoxides with the same number of C-atoms in the molecule as in the starting paraffin).

The further decomposition of these secondary and primary hydroperoxides in the course of the oxidative process proceeds according to schemes II and III given above, i.e., to some extent (greater for primary and lesser for secondary hydroperoxides) according to equations (1) and (2). Confirmation of this may be provided, in particular, by the fact noted above of the formation, during oxidation of individual paraffins, of a certain amount of acids with the same carbon skeleton (during oxidation of ketones, acids are formed with a smaller number of C-atoms in the molecule than in the starting compound), and, moreover, by the repeatedly observed presence, to a known extent, of H_2, as well as methane and its nearest homologues, in the gases of liquid-phase oxidation of paraffinic hydrocarbons.

Taking all this into account, the sequence of formation of molecular products in the slow oxidation by O_2 of n-alkanes in the liquid phase at moderate temperatures may be represented in the following general form:

Scheme IV

```
                                               Esters  \rightarrow Further
                                                 ↑         products
                                      \rightarrow Alcohols

                                                +O_{2} \rightarrow H_{2}O_{2}
Hydrocarbon   +nO_{2}  \rightarrow Hydroperoxides   \rightarrow Carbonyl
                                              compounds

                                      ↓              +O_{2}
                                    H_{2}O             ↓
                           \rightarrow RH*              Acids    \rightarrow Further
                                                  products
```

* Here: R—H or a hydrocarbon radical.

This scheme reflects the latest experimental data showing that carboxylic acids are formed in the course of oxidative transformations of n-alkanes not only by oxidation of carbonyl compounds formed beforehand, but also directly as a result of the decomposition of the initially appearing alkyl hydroperoxides–secondary, primary, and also polyatomic ones, as was established earlier in the case of the decomposition of diisoamyl dihydroperoxide ([23]); it also includes the view that the relatively stable products formed (alcohols, acids, esters, etc.) may, even under comparatively mild conditions, undergo further transformations in the medium of the oxidizing hydrocarbon (coupled reactions of oxidation, decomposition, etc.).

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Received
30 VI 1964

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