INFLUENCE OF SOLVENTS ON THE RADICAL DECOMPOSITION OF KETOHYDROPEROXIDE

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As a result of investigations conducted in recent years, it has been established that the medium influences the rate of radical reactions [1-5]. Thus, for example, it has been shown that the rate constants of reactions of radicals in processes of oxidation (reactions of chain propagation \( \text{RO}_2^+ + \text{RH} \rightarrow \text{ROOH} + \text{R}^+ \) and termination \( \text{RO}_2^+ + \text{RO}_2 \rightarrow \)) are influenced by the dielectric constant of the medium and the ability of peroxide radicals to form hydrogen bonds with the solvent molecules (water, alcohols).

There is also information that the composition of the medium has a substantial effect upon the rate of formation of radicals in the decomposition of peroxides [6-8]. Thus, the alcohols and acids accumulated in the process of oxidation form complexes with hydroperoxides through hydrogen bonds. The decomposition of these complexes into free radicals occurs at a greater rate than in the case of the decomposition of the free hydroperoxide.

The introduction of a solvent may evidently have a substantial influence upon the radical decomposition of hydroperoxides, changing the rate of formation of such complexes.

EXPERIMENTAL

In this work we investigated the influence of the solvent—benzene on the rate of formation of radicals in the decomposition of hydroperoxide formed in the oxidation of methyl ethyl ketone. The ketohydroperoxide was produced in the low-temperature (25-40°) oxidation of methyl ethyl ketone. Under these conditions the hydroperoxide is rather stable and is the only reaction product [9]. Decomposition of methyl ethyl ketone hydroperoxide was studied in a glass reactor at 70° in a stream of air according to the intensity of the chemiluminescence due to recombination of the radicals formed [10]. In parallel experiments the change in the concentration of the ketohydroperoxide was determined by chemical analysis. The presence of oxygen has practically no effect upon the rate of decomposition of the ketohydroperoxide (Fig. 1), which is evidently due to the fact that the rate of decomposition of the ketohydroperoxide substantially exceeds the rate of its formation under the given conditions.

The activation energy of the decomposition of the hydroperoxide was determined from the dependence of the luminescence intensity upon the temperature [10] in the region of 20-60°, while the reaction rate is low and consumption of the hydroperoxide during the experiment can be neglected. For the experiment we used methyl ethyl ketone and "scintillation" benzene, freshly distilled on a column (30 theoretical plates). The kinetic curves of consumption of the ketohydroperoxide in methyl ethyl ketone solution, constructed according to the data of chemiluminescence (1) and according to the results of a chemical determination of the concentration of the hydroperoxide (2), are cited in Fig. 2. The nature of these curves and their semi-logarithmic plots (1', 1", and 2') varies substantially. Curve 1 consists of two portions; moreover, the rate of consumption of the hydroperoxide on the first portion \( (k = 2 \cdot 10^{-4} \text{ sec}^{-1}) \) is substantially greater than on the second \( (k = 2.3 \cdot 10^{-5} \text{ sec}^{-1}) \). From the curves cited in Fig. 2 it follows that the hydroperoxide is consumed with a rate constant \( k = 2.3 \cdot 10^{-5} \text{ sec}^{-1} \), equal to the rate constant of the reaction on the second portion of curve 1. Thus, a comparison of curves 1 and 2 permits us to assume that in the low-temperature oxidation of methyl ethyl ketone, two hydroperoxides are formed in the system. The first, less stable, is accumulated in small amounts, indetectable by chemical analysis, but registered by chemiluminescence (first portion of curve 1). The second hydroperoxide is more stable, comprises the bulk of the hydroperoxide observed during oxidation, and evidently represents an \( \alpha \)-ketohydroperoxide [6, 9, 11].

The possibility of detecting small quantities of reactive hydroperoxides by chemiluminescence in the presence of substantially larger amounts of more stable hydroperoxides may be illustrated in the following way. The luminescence intensity in the presence of the two hydroperoxides is equal to

$$ I = I_1 + I_2; \quad I_1 = \chi_1 k_1 [\text{ROOH}]_0 e^{-k_1 [\text{ROOH}]_0 t}, $$

$$ I_2 = \chi_2 k_2 [\text{X}]_0 e^{-k_2 [\text{X}]_0 t} $$

where $\chi_1$ and $\chi_2$ are the luminescence yields. For this

$$ \ln I_1 = \ln \chi_1 k_1 [\text{ROOH}]_0 - k_1 [\text{ROOH}]_0 t $$

$$ \ln I_2 = \ln \chi_2 k_2 [\text{X}]_0 - k_2 [\text{X}]_0 t $$

If $[\text{ROOH}]_0 > [\text{X}]_0$ (for example, $[\text{ROOH}]_0 = 10^{-2}$ M, when $[\text{X}]_0 = 10^{-3}$ M), then ROOH is less reactive than X($k_1 \text{ROOH} = 10^{-5}$ sec$^{-1}$, while $k_1 \text{X} = 10^{-4}$ sec$^{-1}$), then assuming $\chi_1 = \chi_2 = 1$, we obtain the following values of the chemiluminescence intensities $I_1$ and $I_2$

<table>
<thead>
<tr>
<th>t (sec)</th>
<th>$\ln [\text{ROOH}]_0$</th>
<th>$\ln [\text{X}]_0$</th>
<th>$\ln I_1$</th>
<th>$\ln I_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-2</td>
<td>-3</td>
<td>-7</td>
<td>-7</td>
</tr>
<tr>
<td>$10^3$</td>
<td>-2,01</td>
<td>-3,1</td>
<td>-7,01</td>
<td>-7,1</td>
</tr>
<tr>
<td>$10^4$</td>
<td>-2,13</td>
<td>-4,0</td>
<td>-7,1</td>
<td>-8,0</td>
</tr>
<tr>
<td>$10^5$</td>
<td>-3,03</td>
<td>-13,0</td>
<td>-8,0</td>
<td>-17,0</td>
</tr>
</tbody>
</table>

The chemiluminescence intensities are practically the same. At the same time, chemical methods do not permit the detection of small quantities of the peroxide X, and the curve of consumption of hydroperoxides corresponds to the kinetics of the decomposition only of the ketohydroperoxide.

The values of the rate constants of the decomposition of the hydroperoxide X and the ketohydroperoxide do not depend upon their concentration (Fig. 3). From this it can be concluded that under the conditions of our experiments, there is no chain decomposition of hydroperoxides, induced by free radicals.

The hydroperoxides are consumed, forming free radicals (branching of chains) or molecular products (molecular decomposition).

To estimate the proportion of the reaction of chain branching in the total rate of decomposition of hydroperoxides, we measured the rate of oxidation of methyl ethyl ketone, containing the ketohydroperoxide. Since the rate of oxidation [9]

$$ w = \frac{k_2}{\sqrt{v_q [\text{RH}]_0}} \sqrt{\bar{w}_0} $$

and knowing $k_0/\sqrt{k_q}$ [1-3, 12], we can determine $w_q = 2k_1 [\text{ROOH}]_0$.

By comparing the value of $k_1$ obtained by this method with $k_1$ determined from curve 2 (see Fig. 2), it was shown that 85-90% of the $\alpha$-ketohydroperoxide breaks down, forming free radicals. Consequently, the curves of consumption of ketohydroperoxide measured with the aid of chemiluminescence characterize the rate of formation of radicals in such systems.

In our previous studies, when the decomposition of hydroperoxides was studied in a metallic reactor [13], only ~30% of the hydroperoxide broke down into radicals, and 70% was converted to molecular reaction products. This is evidence of a great role of heterogeneous factors in the mechanism of the decomposition of hydroperoxides.

To investigate the influence of solvents on the mechanism of radical formation, we measured the rate of decomposition of the ketohydroperoxide in a 1:1 methyl ethyl ketone:benzene solution (Fig. 4). The nature of the curves remains the same as in pure methyl ethyl ketone (see Fig. 2). With increasing...