FORMATION OF FREE RADICALS IN ACID-CATALYZED DECOMPOSITION OF DI-tert-BUTYL PEROXIDE

V. M. Solyanikov and L. V. Petrov


Mineral acids (HCl, HClO₄, H₂SO₄) in alcohol medium function as catalysts for the heterolytic and homolytic decomposition of hydroperoxides [1]. An acceleration in the homolytic decomposition of alkyl and acyl peroxides is not observed under these conditions. We recorded the formation of free radicals when di-tert-butyl peroxide (DTBP) was decomposed in CH₃CN in the presence of strong protic (HClO₄) and Lewis (BF₃·THF complex) acids. The present communication is devoted to ascertaining the manner in which the radicals are formed.

EXPERIMENTAL METHOD

The employed compounds (DTBP, BF₃·THF, styrene, 70% HClO₄) were purified by fractional distillation in vacuo. The CH₃CN was purified by azeotropic distillation with ethanol, followed by drying over P₂O₅ and fractional distillation. The formation of free radicals was judged by the rate of the radical-chain oxidation of styrene in CH₃CN solution, in the simultaneous presence of the acid and DTBP (60°C). In a two-section Rittenberg vessel [2], connected to a manometer setup, the DTBP and the acid were heated separately in an acetonitrile solution of styrene. When the desired temperature was reached the sections were connected by shaking the vessel, the reactants were mixed, and the rate of oxygen absorption was measured. To analyze for the products of the acid decomposition of DTBP the decomposition reaction was run in a reactor, from which samples were removed during experiment and analyzed by GLC. A 900 × 3 mm column, packed with 30% dinonyl phthalate deposited on Celite-545 (50°), was used for the analysis.

DISCUSSION OF RESULTS

The oxidation rate is given in Fig. 1, from which it can be seen that the addition of acid sharply increases the formation rate of the free radicals in the presence of DTBP. Without it, the styrene is not oxidized in the presence of acid alone. The addition of water hinders the formation of the radicals (see Fig. 1, curve 2'). This is evidently due to a decrease in the acidity of the medium. Iodometric analysis of samples from the reactor indicated the rapid formation in this system of a form of peroxide that liberates iodine from KI in CH₃COOH medium (DTBP does not oxidize I⁻ to I₂). The formation of this form of peroxide was also confirmed by GLC analysis, and specifically the identification of tert-butyl hydroperoxide (TBHP) in the reaction product of DTBP with HClO₄. The rate of forming TBHP is given in Table 1: a steady-state concentration of TBHP in the DTBP solution is established in practically 5-10 min. In addition, isobutylene (identified by the Kaufmann–Baltes method [3]) was found in the products of the acid-catalyzed decomposition of DTBP. In special experiments we established that isobutylene is absent in the products obtained by the decomposition of TBHP using HClO₄ or BF₃·THF, i.e., the isobutylene is most probably formed directly from DTBP. In the material balance experiment it was found that 0.023 mole/liter of TBHP and 0.022 mole/liter of isobutylene were formed per 0.028 mole/liter of decomposed DTBP, i.e., roughly one molecule of TBHP and one molecule of isobutylene are formed per molecule of decomposed DTBP. As a result, in the studied system the homolysis of the formed TBHP under the influence of a Brønsted or Lewis acid serves as an indicator of the DTBP transformations.


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Fig. 1. Kinetic curves of oxygen absorption at a styrene concentration in CH$_3$CN of 0.522 mole/liter, 60°. 1) [DTBP] = 0.36 mole/liter, without acid; 2) [DTBP] = 0.36, [HClO$_4$] = 0.1 mole/liter; 2') [DTBP] = 0.36, [HClO$_4$] = 0.1, [H$_2$O] = 0.4 mole/liter; 3) [DTBP] = 0.36, [BF$_3$·THF] = 5 · 10$^{-2}$ mole/liter.

TABLE 1. Rate of Forming tert-Butyl Hydroperoxide from Di-tert-butyl Peroxide [HClO$_4$] = 0.01 mole/liter 60°.

<table>
<thead>
<tr>
<th>Time, min</th>
<th>Concentration, mole/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DTBP</td>
</tr>
<tr>
<td>0</td>
<td>0.385</td>
</tr>
<tr>
<td>5</td>
<td>0.367</td>
</tr>
<tr>
<td>15</td>
<td>0.363</td>
</tr>
<tr>
<td>30</td>
<td>0.365</td>
</tr>
<tr>
<td>60</td>
<td>0.355</td>
</tr>
</tbody>
</table>

Direct experiments on the oxidation of styrene in the presence of tert-butyl hydroperoxide and either HClO$_4$ or BF$_3$·THF confirmed the fact that here the hydroperoxide decomposes rapidly with the escape of free radicals into space. Consequently, the scheme for the transformations of DTBP can be depicted in the following manner.

\[
\begin{align*}
\text{H}^+ & \quad (\text{CH}_3)_3\text{COOC(CH}_3)_3 \rightarrow (\text{CH}_3)_3\text{COOH} + (\text{CH}_3)_2\text{C}^+ \\
(\text{CH}_3)_2\text{C}^+ & \rightarrow \text{H}^+ + \text{CH}_3 = \text{C(CH}_3)_3 \\
(\text{CH}_3)_3\text{COOH} & \rightarrow \text{H}^+ \quad \text{free radicals} + \text{molecular products}
\end{align*}
\]

Our results are in good agreement with the data given in [4], where the iodometric method is recommended for the determination of DTBP, with its prior decomposition in the presence of acid. At the same time, it is known that alkenes in the presence of protic acids mildly alkylate hydroperoxides to give peroxides [5], i.e., acid also catalyzes the reaction that is the reverse of the reaction for the acid decomposition of DTBP.

CONCLUSIONS

Di-tert-butyl peroxide under the influence of protic and aprotic acids is converted to isobutylene and tert-butyl hydroperoxide. The formation of free radicals occurs as the result of the acid-catalyzed homolysis of the hydroperoxide.