THERMAL DECOMPOSITION OF THE DIMETHYL ESTER OF PEROXYDIPHTHALIC ACID

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The thermal decomposition of benzoyl peroxide in organic solvents has been investigated in detail by a number of authors [1-4]. The decomposition of other aroyl peroxides containing functional or alkyl groups in the benzene ring has been considerably less studied. It was established that the benzoyloxy radicals, possessing substituents in the o-position, generated from certain peroxides, are inclined to undergo various rearrangements. Thus, the formation of individual products in the decomposition of o-tolylbenzoyl and o-benzoylbenzoyl peroxides can be explained by intramolecular transfer of hydrogen atoms in the corresponding benzoyloxy radicals [5]. The thermal decomposition of o-phenoxybenzoyl peroxide is accompanied by a rearrangement of the o-phenoxybenzoyl radicals that arise to o-(carbophenoxy)-phenoxy radicals [6]. 3,4-Benzocoumarin is formed from o-phenylbenzoyl peroxide as a result of homolytic cyclization of o-phenylenzoyl radicals [5].

This work was devoted to an investigation of the thermal decomposition of the dimethyl ester of peroxydiphthalic acid (DEPA) in solution; peroxydiphthalic acid itself is practically insoluble in organic solvents. The basic reactions products were identified, and the reaction kinetics in benzene and acetic acid was studied. According to the kinetic data, the decomposition of DEPA obeys a first-order equation with respect to the peroxide (Figs. 1 and 2). In acetic acid the reaction proceeds at a somewhat higher rate than in benzene, which is evidenced by the values of the rate constants at the temperature 80°, $1.97 \times 10^{-4}$ and $1.47 \times 10^{-4}$ sec$^{-1}$, respectively (Table 1). The activation energy of the decomposition in benzene is 24.0 kcal/mole, and in acetic acid 27.5 kcal/mole. It should be noted that the activation energy of the decomposition of benzoyl peroxide in benzene is 29.6 [7] and 31.0 kcal/mole [8] – it differs appreciably from the value that we found for DEPA.

The data obtained, in particular, the composition and structure of the reaction products (Table 2), permit us to assume that at the first step of the decomposition of DEPA there is a homolytic cleavage of

\[ \begin{align*}
\text{H}_2\text{C} & \quad \text{C} \quad \text{O} \\
\text{O} & \quad \text{C} \quad \text{C} \\
\text{H}_2\text{C} & \quad \text{C} \quad \text{O}
\end{align*} \]

\[ \begin{align*}
\text{H}_2\text{C} & \quad \text{C} \quad \text{O} \\
\text{O} & \quad \text{C} \quad \text{C} \\
\text{H}_2\text{C} & \quad \text{C} \quad \text{O}
\end{align*} \]

Fig. 1. Semilogarithmic plots of the kinetic curves of the decomposition of the dimethyl ester of peroxydiphthalic acid in acetic acid.

Fig. 2. Semilogarithmic plots of the kinetic curves of the decomposition of the dimethyl ester of peroxydiphthalic acid in benzene.

the O – O bond with the formation of o- (carbomethoxy)benzoyloxy radicals (I)

\[
\begin{align*}
\text{COOCH}_3 & \quad \text{COO}^- \\
\text{COO}^- & \quad \text{COOCH}_3
\end{align*}
\]

(I)

At the temperature 80° and DEPA concentration 0.045 M, these radicals undergo decarboxylation to a substantial degree: in acetic acid 1.35 moles of carbon dioxide per mole of the peroxide are liberated, and in benzene 1.16 moles of carbon dioxide

\[
\begin{align*}
\text{COOCH}_3 & \quad \text{COO}^- \\
\text{COO}^- & \quad \text{COOCH}_3 + \text{CO}_2
\end{align*}
\]

(II)

The formation of other gaseous substances does not occur. Phthalic anhydride was detected somewhat unexpectedly in the decomposition products. Its formation can be explained if we assume that the radicals (I) are capable of cyclization with elimination of a methoxy radical

\[
\begin{align*}
\text{COOCH}_3 & \quad \text{COO}^- \\
\text{COO}^- & \quad \text{COOCH}_3 + \text{CH}_3\text{O}
\end{align*}
\]

(3)

The probability of such cyclization is confirmed by a qualitative identification of methanol in the reaction mixture (by the method of mass spectrometry on an MI-1305 instrument according to the characteristic peaks of the ions with mass numbers 32 and 31). The latter is readily obtained on account of stripping of hydrogen atoms from the solvent by methoxy radicals [9]. However, reaction (3) cannot be considered a priori as the only pathway of synthesis of phthalic anhydride and methanol from DEPA. Together with the homolytic cyclization of radicals (I), we should also have assumed the possibility of occurrence of reactions (4) and (5)

\[
\begin{align*}
\text{COOCH}_3 & \quad \text{COO}^- \\
\text{COO}^- & \quad \text{COOCH}_3 + \text{R}\text{H} + \text{R}'
\end{align*}
\]

(4)

\[
\begin{align*}
\text{COOCH}_3 & \quad \text{COO}^- \\
\text{COO}^- & \quad \text{COOCH}_3 + \text{CH}_3\text{OH}
\end{align*}
\]

(5)

Our investigations permitted us to establish that under the experimental conditions that we used, methanol and phthalic anhydride are not formed from the monomethyl ester of phthalic acid, i.e., reaction (5) does not take place. In addition to participation in monomolecular processes of decarboxylation and cyclization, radical (I) is also capable of interacting with the solvent.

### Table 1. Rate Constants of the Decomposition of the Dimethyl Ester of Peroxydiphthalic Acid in Acetic Acid and Benzene

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Reaction rate constant k·10⁴</th>
<th>acetate acid</th>
<th>benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>95.0</td>
<td>10.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90.0</td>
<td>5.62</td>
<td></td>
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</tr>
<tr>
<td>85.0</td>
<td>3.40</td>
<td></td>
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</tr>
<tr>
<td>80.0</td>
<td>1.97</td>
<td>1.47</td>
<td></td>
</tr>
<tr>
<td>75.0</td>
<td>0.90</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>72.0</td>
<td>0.63</td>
<td>0.52</td>
<td></td>
</tr>
</tbody>
</table>

E, kcal/mole | 27.5 | 24.0

### Table 2. Yield of Decomposition Products of the Dimethyl Ester of Peroxydiphthalic Acid, Moles per Mole of the Peroxide

<table>
<thead>
<tr>
<th>Solvent</th>
<th>T, °C</th>
<th>Carbon dioxide</th>
<th>Phthalic anhydride</th>
<th>Methyl ester of benzoic acid</th>
<th>Dimethyl ester of phthalic acid</th>
<th>Methyl ester of p-phenylenedicarboxylic acid</th>
<th>Methyl ester of succinic acid</th>
<th>Dimethyl ester of phthalic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene,</td>
<td>80</td>
<td>1.16</td>
<td>0.556</td>
<td>0.240</td>
<td>0.220</td>
<td>0.557</td>
<td>0.001</td>
<td>0.085</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>80</td>
<td>1.35</td>
<td>0.236</td>
<td>0.970</td>
<td>0.096</td>
<td>0.557</td>
<td>0.001</td>
<td>0.085</td>
</tr>
</tbody>
</table>