3. In the hydrochloric acid and sulfuric acid solutions in question here (up to 74.9% H₂SO₄), the hydrolysis of ethyl isovalerate proceeds through an activated complex containing one un-ionized ester molecule and one hydronium ion carrying at least one solvation water molecule. The water molecule functions here as a nucleophilic agent.

4. The data obtained can be interpreted quantitatively by assuming that ionization results in the formation of a protonized form of the ester and an unreactive complex in which the carbonyl group oxygen is bound to the hydronium ion.

5. Hydrolysis proceeds through the protonized form of the ester in sulfuric acid solutions with concentrations in excess of 74.9%.

**LITERATURE CITED**


**ACID CATALYSIS IN RADICAL HYDROPEROXIDE DECOMPOSITION**

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**UDC 541.123; 541.515; 542.92; 541.459**

There are two distinctly different mechanisms for catalyzing radical hydroperoxide decomposition [1-5], the one involving weak mineral acids [3-5] and the other weak carboxyl acids [1, 2]. Since there have been few studies of acid catalysis of radical hydroperoxide decomposition, it seemed of interest to investigate the effect of organic acid acidity on radical formation. Since mineral acid catalysis has been studied only in secondary alcoholic solution [3-5], the present work was carried out with methyl ethyl ketone (MEK) and acetic acid.

**EXPERIMENTAL**

The techniques of determining the rate of chain substrate oxidation through measurement of O₂ absorption, and the method of calculating the rate of free-radical formation, have already been described in [3]. The compounds used in this work had been purified with especial care. Vacuum distillation was used to purify the CF₃COOH, cumyl hydroperoxide (CHP), tertiary amyl hydroperoxide (TAHP), and aqueous H₂O₂. The final purity of the CHP was 99%, and that of the TAHP, 86%; the distilled perhydrol contained ~40% H₂O₂, the latter determined iodometrically. H₂SO₄ and HClO₄ were purified by the methods of [4]. Glacial CH₃COOH was distilled through a fractionating column at atmospheric pressure. The cumene was repeatedly extracted with concentrated H₂SO₄, washed with water and a soda solution, dried over CaCl₂, and then distilled over Na. The cyclohexane was passed through a column loaded with Al₂O₃, and then distilled over Na. CC₁₃COOH was recrystallized from isooctane, and then vacuum dried at ~20°C. Pure grade CH₂CICOOH was used without further purification, after being vacuum dried.

TABLE 1. Variation of the Rate of Oxidation of Methyl Ethyl Ketone with the Acid Concentration
([H₂O] = 10 vol. %, [H₂O₂] = 0.56 mole / liter, 70°C)

<table>
<thead>
<tr>
<th>[H₂SO₄] tetran, mole / liter</th>
<th>W. 10⁻⁶, mole / (liter·sec)</th>
<th>[HClO₄] tetran, mole / liter</th>
<th>W. 10⁻⁶, mole / (liter·sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.15</td>
<td>0</td>
<td>0.45</td>
</tr>
<tr>
<td>1.3</td>
<td>2.6</td>
<td>1.0</td>
<td>2.7</td>
</tr>
<tr>
<td>2</td>
<td>3.9</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>3.8</td>
<td>3.5</td>
<td>3</td>
<td>6.6</td>
</tr>
<tr>
<td>4.5</td>
<td>20</td>
<td>4</td>
<td>10</td>
</tr>
</tbody>
</table>

DISCUSSION OF RESULTS

In the presence of TAHP trichloracetic, sulfuric, and perchloric acids catalyzed the oxidation of cyclohexene (20%) in CH₃COOH (Fig. 1). Studies on azoisobutyronitrile (AIBN) initiation of the cyclohexene oxidation in CH₃COOH showed the oxidation rate W to be proportional to √W₁. Thus, √W₁ = 4.5 · 10⁻⁴ at W = 9 · 10⁻⁶, √W₁ = 6.5 · 10⁻⁴ at W = 14 · 10⁻⁶, and √W₁ = 9 · 10⁻⁴ at W = 18 · 10⁻⁶, W and W₁ being measured in mole/liter·sec. The presence of sulfuric, perchloric, and trichloracetic acid had no effect on the rate of the AIBN-initiated oxidation. Thus, the increase of W with increasing acid concentration observed in the hydroperoxide-initiated reaction was a reflection of enhanced radical breakdown.

The present theory of proton catalysis in radical hydroperoxide breakdown suggests that acid catalytic activity in radical formation increases with the protonic strength of the acid (cf. Fig. 1). Comparative experiments with [TAHP] = 0.02 mole / liter and the concentration of the halogenated acetic acid equal to 0.31 mole / liter showed the oxidation rate to be 0.37 · 10⁻⁶ mole / liter·sec in the absence of acid, 0.88 · 10⁻⁶ mole / liter·sec in the presence of CH₂CICOOH, 4.5 · 10⁻⁵ mole / liter·sec in the presence of CCl₃COOH, and 8 · 10⁻⁵ mole / liter·sec in the presence of CF₃COOH. The ratio of initiation rates was exactly equal to the ratio of the square roots of the observed reaction rates, namely, 1 : 6 : 144 : 440. The experimental data showed the catalytic activity of the acids to fall off in the order HClO₄ > H₂SO₄ > CF₃COOH > CCl₃COOH > CH₂CICOOH > CH₃COOH.

Thus, there was a clear-cut correlation between the protonic strength of the acid (regardless of its nature) and the activity of the acid in catalyzing hydroperoxide radical formation. The catalyzing action of the halogen-substituted acetic acids appeared, moreover, at concentrations (0.31 mole / liter) much lower than that of the CH₃COOH (80%, 14 moles / liter CH₃COOH) which functioned as the solvent in these experiments. If hydroperoxide free-radical formation proceeded here solely through the

\[
\begin{align*}
R'\mathrm{C} + \mathrm{ROOH} & \rightleftharpoons R'\mathrm{C} + \mathrm{ROH} \\
\mathrm{O} - \mathrm{H} - \mathrm{O} & \rightarrow \mathrm{R'C} + \mathrm{HO} - \mathrm{RO}'' \quad [1]
\end{align*}
\]

or the

\[
\begin{align*}
R'\mathrm{C} + \mathrm{ROOH} & \rightleftharpoons R'\mathrm{C} + \mathrm{ROH} \\
\mathrm{O} - \mathrm{H} - \mathrm{O} & \rightarrow \mathrm{R'C} + \mathrm{H}_2\mathrm{O} + \mathrm{RO}''
\end{align*}
\]

mechanism, it would be difficult to explain the appearance of catalytic activity by the halogen-substituted acetic acids in cases where the ROOH...CH₃COOH complex concentration was much higher than the concentration of the ROOH...halogen-substituted acid associates. From this it could be concluded that a protonization mechanism of radical formation must come into play even with the halogen-substituted organic acids.

Two conclusions can be drawn from the studies of radical hydroperoxide breakdown under the action of sulfuric and hydrochloric acids in MEK containing 10% water (Figs. 2-4, Table 1).

1. The activity of H₂SO₄ and HCl in radical hydroperoxide breakdown in a polar medium (aqueous ketone solution) does not depend on the nature of the anion, but is related to the degree of acid dissociation.

2. Strong acids catalyze the radical decomposition of CHP (cf. Figs. 3 and 4). On the other hand, the products resulting from acid CHP cleavage are consistent with the supposition that this reaction follows an ionic reaction mechanism [6].