Decomposition of Aromatic Peroxyacids in Aqueous Alkali

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A study has been made of the uncatalyzed decomposition of aromatic peroxyacids in aqueous solution, particular attention having been paid to the effects of pH and peroxyacid structure on the rates of reaction. Second-order kinetics were observed with maximum rates at 50% dissociation of the peroxyacid. It has been shown that the rate-determining step is the attack of the peroxyacid anion on the unionized peroxyacid to form an intermediate which decomposes rapidly to give the parent carboxylic acid and oxygen as the main reaction products. A comparison is drawn with the decomposition kinetics of analogous inorganic peroxycompounds and a general mechanism proposed.

Peroxyacids have been widely used as oxidizing agents in non-aqueous media, and the kinetics of their reactions with unsaturated linkages, ketones and nitrogen- and sulphur-containing compounds have been thoroughly investigated. However, investigations in aqueous solution have been comparatively few. In particular, studies of the decomposition of peroxyacids appear to have been confined principally to the inorganic materials, peroxymonosulphuric acid and hydrogen peroxide; cursory investigations of the uncatalyzed decomposition of hydroperoxides in aqueous alkali have also been reported. This paper describes a study of the decomposition of aromatic peroxyacids in aqueous solution, particular attention being paid to the effects of pH and peroxyacid structure on the rates of reaction. The results from this investigation suggest that the mechanism of decomposition in aqueous alkaline solution is the same both for organic and inorganic peroxyacids.

EXPERIMENTAL

MATERIALS

The aromatic peroxyacids were prepared by the action of sodium methoxide on the symmetrical diaroyl peroxide, which gave products of 80-90% purity. Further purification was affected by sublimation under reduced pressure when the only impurity remaining was the parent carboxylic acid.

Preliminary work showed that inorganic anions (e.g., borate) and heavy metal cations can accelerate the decomposition rate. The uncatalyzed decompositions were investigated in solutions of sodium hydroxide in redistilled water, to which disodium ethylenediaminetetra-acetic acid (E.D.T.A.) had been added to sequester traces of heavy metal ions, shown to be present by polarographic analysis.

DISSOCIATION CONSTANTS

The pK values of the substituted aromatic peroxyacids were determined by potentiometric titration. Since it proved impossible to isolate the peroxyacids free from traces of the parent carboxylic acid, the latter was added in fixed quantities and the pK values of both acids determined simultaneously. The good agreement between the values obtained for the pKs of the parent acid and those given in the literature confirmed the accuracy of our measurements.

DECOMPOSITION OF THE PEROXYACIDS

The rates of decomposition of the peroxyacids in aqueous alkaline solution were followed in carefully cleaned glass flasks, immersed in a constant temperature bath (±0.1°C).
A solution of the peroxyacid in redistilled water, containing E.D.T.A., was filtered and transferred to the reaction flask. The pH of the reaction mixture was adjusted to the required value by the addition of sodium hydroxide solution and monitored throughout the experiment with a glass electrode, the pH being kept constant to ±0.03 unit by the further addition of alkali. The volumetric error introduced was negligible for the first 1-2 h of the reaction. After allowing the reaction mixture to come to temperature equilibrium, aliquots were removed at specific time intervals, pipetted into glacial acetic acid containing ice and solid carbon dioxide and the peroxyacid estimated iodometrically.14

PRODUCT SEARCH

Although preliminary experiments indicated that the peroxyacid gave the parent carboxylic acid in yields of greater than 90%, when allowed to decompose completely in aqueous alkaline solution, small quantities of diaroyl peroxide were also detected. To determine accurately the proportions of these two materials formed during decomposition, a solution of peroxyacid was allowed to decompose at a fixed pH for 48 h. The mixture was then made strongly alkaline and the diaroyl peroxide extracted with chloroform. The extracts were dried, filtered and saturated with carbon dioxide to exclude oxygen. Saturated potassium iodide solution and a solution of ferric chloride in acetic acid were added and after standing 15 min, the free iodine estimated with sodium thiosulphate solution.

The parent carboxylic acid and the unchanged peroxyacid were then isolated by acidification of the aqueous layer with strong sulphuric acid and extraction with ether. The extracts were dried, filtered, evaporated to dryness, dissolved in a fixed quantity of water and titrated potentiometrically with sodium hydroxide to the neutralization point of the carboxylic acid. The solution was then re-acidified and the peroxyacid determined iodometrically.14

RESULTS

RATES OF DECOMPOSITION

At fixed pH and temperature it was found that the peroxyacid was destroyed by a second-order process, and the observed second-order rate constant \( k_0 \) was obtained from the slope of the line obtained by plotting the reciprocal of the peroxyacid concentration against time. The value of \( k_0 \) was only marginally changed by the nature of the reaction vessel (polythene or glass), or by the addition of increasing quantities of E.D.T.A. or the parent carboxylic acid. However, the pH of the system had a marked effect on the rate of decomposition, as shown in fig. 1, where \( \log k_0 \) for peroxybenzoic acid is plotted against pH. Errors in \( k_0 \) and pH are represented by the rectangles surrounding each point. It was found that the decomposition rate reached a maximum when the pH of the reaction mixture corresponded to the pK of the peroxyacid. The rate of decomposition was extremely small for peroxyacid dissociations close to 0 or 100%, confirming that catalytic decomposition was

<table>
<thead>
<tr>
<th>Substituted peroxybenzoic acid</th>
<th>pK 25°C</th>
<th>pK 35°C</th>
<th>pK 45°C</th>
<th>( k_0 ) at 50% dissociation ( \times 10^3 ) l./mole sec</th>
<th>( k_0 ) at 45°C ( \times 10^3 ) l./mole sec</th>
<th>Activation energy (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-methoxy-</td>
<td>8.07</td>
<td></td>
<td></td>
<td>4.9</td>
<td>9.8</td>
<td>16.6</td>
</tr>
<tr>
<td>p-methyl-</td>
<td>7.95</td>
<td>7.80</td>
<td>7.73</td>
<td>4.7</td>
<td>10.9</td>
<td>27.3</td>
</tr>
<tr>
<td>unsubst.</td>
<td>7.78</td>
<td>7.74</td>
<td>7.63</td>
<td>4.5</td>
<td>11.7</td>
<td>27.7</td>
</tr>
<tr>
<td>p-fluoro-</td>
<td>7.76</td>
<td></td>
<td></td>
<td>5.2</td>
<td>10.4</td>
<td>17.3</td>
</tr>
<tr>
<td>p-chloro-</td>
<td>7.67</td>
<td></td>
<td></td>
<td>7.5</td>
<td>15.0</td>
<td>17.0</td>
</tr>
<tr>
<td>m-chloro-</td>
<td>7.60</td>
<td>7.46</td>
<td>7.37</td>
<td>7.7</td>
<td>18.7</td>
<td>46.4</td>
</tr>
<tr>
<td>p-nitro-</td>
<td>7.29</td>
<td></td>
<td></td>
<td>10.6</td>
<td>21.2</td>
<td></td>
</tr>
</tbody>
</table>

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negligible. The values of $k_0$ for a series of substituted peroxybenzoic acids were determined under conditions of 50 % dissociation at different temperatures and the combined results are shown in the table.

![Graph showing variation of log10 $k_0$ for peroxybenzoic acid with pH at 25°C.]

**PRODUCTS OF DECOMPOSITION**

The products remaining after decomposition of peroxybenzoic acid were shown to be benzoic acid and dibenzoyl peroxide only. The yields of benzoic acid were found to be 99.4, 95.6 and 99.9 % in terms of peroxyacid consumed at pH's of 7, 8 and 9 respectively. The maximum quantity of diaroyl peroxide was produced when the rate of decomposition was a maximum, but never exceeded 5 %.

**DISCUSSION**

**KINETICS OF DECOMPOSITION**

The peroxybenzoic acids decompose by a second-order process, the rate of which has a maximum value at a pH corresponding to the pK of the peroxyacid, and is extremely small at peroxyacid dissociations close to 0 and 100 %. It may be inferred, therefore, that both the peroxyacid anion and unionized peroxyacid are present at the intermediate state, and that the second-order process represents the main uncatalyzed reaction. The decomposition process may be represented:

$$RCo_3^- + RCo_3H^+ \rightarrow \text{intermediate} \rightarrow \text{products},$$

where the "reactants" are related by the equilibrium,

$$RCo_3H + H_2O \equiv RCo_3^- + H_3O^+.$$ (1)
At constant pH,

\[ \frac{[RCO_3H]}{[RCO_3^-]} = \frac{[H_3O^+]}{K} = A \text{ (constant).} \]  

(2)

If the overall rate is determined by the formation of the intermediate, and at time \( t \), \( x \) moles of each reactant have decomposed, the rate of reaction is given by

\[ \frac{\delta x}{\delta t} = k_2[RCO_3^-][RCO_3H]. \]  

(3)

Let \( T_0 \) be the initial concentration of \( RCO_3H \) plus \( RCO_3^- \), and \( T \) the concentration at time \( t \). Then,

\[ T = [RCO_3^-] + [RCO_3H], \]  

(4)

and

\[ T = T_0 - 2x. \]  

(5)

From (2) and (4),

\[ [RCO_3^-][RCO_3H] = A[RCO_3^-]^2 = AT^2/(1 + A)^2, \]  

(6)

and from (5),

\[ \frac{\delta x}{\delta t} = -\frac{1}{2} \delta T/\delta t. \]  

(7)

From (3), (6) and (7) we obtain

\[ -\frac{\delta T}{\delta t} = 2Ak_2T^2/(1 + A)^2, \]  

(8)

which on integration gives

\[ \frac{1}{T} - \frac{1}{T_0} = \frac{2Ak_2}{(1 + A)^2}t. \]  

(9)

The observed second-order rate constant \( k_0 \) at any pH is, therefore, related to the true rate constant \( k_2 \) as follows:

\[ k_0 = \frac{2A}{(1 + A)^2}k_2. \]  

(10)

Superimposed on the experimental values of \( k_0 \) in fig. 1, is a line calculated using eqn. (10), the value of \( k_2 \) being taken as \( 2k_0 \) at 50% dissociation. Satisfactory agreement is obtained, confirming that eqn. (3) represents the kinetic form of the reaction. Similar agreement was also obtained for the decomposition of p-methyl- and m-chloro-peroxybenzoic acids over a range of pH.

**MECHANISM OF DECOMPOSITION**

It would appear that an intermediate state is formed by the attack of the nucleophilic peroxyacid anion on the electrophilic carbonyl carbon of the unionized peroxyacid.

\[ \begin{align*}
\text{O} & \quad \text{O} & \quad \text{O} \\
\text{R} & \quad \text{C} & \quad \text{H} & \quad \text{R} \\
\text{OOCR} & \quad \text{O} & \quad \text{O} & \quad \text{C} = \text{O} & \quad \text{R}
\end{align*} \]

(11)

The effect of nuclear substituents on the nucleophilicity of the peroxyacid anion is small. The rate of decomposition of the peroxyacid should, therefore, depend to
DECOMPOSITION OF PEROXYACIDS

A greater extent on the electrophilic properties of the carbonyl carbon of the un-ionized peroxyacid. Electron-withdrawing substituents increase this electrophilicity and, as expected, these peroxyacids were found to decompose faster than the unsubstituted acid at a given temperature. Substituents have little effect on the activation energies of the decomposition, which were found to be approximately 17 kcal/mole.

Further support for the mechanism proposed above was obtained by studying the peroxyacid decomposition in a solution containing both p-nitro- and p-methyl-peroxybenzoic acid at a fixed temperature and pH. The decomposition occurred at a faster rate than would be expected if each peroxyacid decomposed individually. This observation suggests that the strongest nucleophile present MeC₆H₇C0ₒ, reacted with the most favoured receptor molecule, NO₂C₆H₄C0₃H₃, as well as its own unionized analogue. The unfavoured reaction of NO₂C₆H₄C0₃H with MeC₆H₇C0₃H, presumably occurred only to a very limited extent.

An intermediate of the type proposed in (11) would be transient, decomposing immediately to the parent carboxylic acid and oxygen via a cyclic intramolecularly hydrogen-bonded form:

\[
\begin{align*}
\text{O} \\
\text{R-}[\text{C-O]+[H-O=O-H} \\
\text{R-C=O}
\end{align*}
\]

The small quantities of diaroyl peroxide detected are thought to arise by the alternative breakdown of the intermediate:

\[
\begin{align*}
\text{O} \\
\text{R-}[\text{C-O]+[H-OH} \\
\text{R-C=O}
\end{align*}
\]

The diaroyl peroxide could have arisen by the recombination of percarboxylate radicals formed by the OH-bond homolysis in the peroxyacid molecule. However, this seems unlikely since acrylonitrile was not polymerized when added to the reaction mixture, showing that a significant number of radicals could not be present.

It has been reported that peroxymonosulphuric acid decomposes by a second-order process, the rate of which is pH dependent and has a maximum value at the pK of the system:

\[
\text{HSO}_5^- + \text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + \text{H}_3\text{O}^+.
\]

Since the reaction was studied in phosphate and carbonate buffers it is quite possible that the inorganic anions present influenced the decomposition rate. Nevertheless, peroxymonosulphuric acid appears to be completely analogous in its uncatalyzed decomposition to the aromatic peroxyacids. Similarly, hydrogen peroxide decomposes at a maximum rate when 50 % ionized:

\[
\text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HO}_2^- + \text{H}_3\text{O}^+.
\]
It seems reasonable to suggest, therefore, that the mechanism of decomposition is the same both for organic and inorganic peroxyacids, and consists of the attack by the nucleophilic peroxyanion on an electrophilic centre in the unionized peroxyacid. The electrophilic centre for the organic peroxyacids has been shown to be the carbonyl carbon atom, which is attacked by the nucleophilic \( RCO_3^- \) ion. There is not enough evidence in the case of peroxymonosulphuric acid and hydrogen peroxide to be certain which atom is attacked by the nucleophilic \( SO_4^{2-} \) and \( HO_2^- \) ions. However, if we assume that the electrophilic centres are sulphur and hydrogen for the peroxy-monosulphuric acid and hydrogen peroxide respectively, then the rapid breakdown of a cyclic intermediate can occur in a manner exactly analogous to that proposed for the aromatic peroxyacids.