Aldehydes are oxidized easily by moist silver oxide or by potassium permanganate solution to the corresponding acids. The mechanism of the permanganate oxidation has some resemblance to the chromic acid oxidation of alcohols (Section 15-6B):

\[
\begin{align*}
\text{R} - \text{C} & \quad \text{[O]} \quad \text{R} - \text{C} \quad \text{O}
\end{align*}
\]

Many aldehydes are oxidized easily by atmospheric oxygen in a radical-chain mechanism. Oxidation of benzenecarbaldehyde to benzenecarboxylic acid has been studied particularly well and involves formation of a peroxy acid as an intermediate. Reaction is initiated by a radical \(\text{\text{R} \cdot}\) which breaks the relatively weak aldehyde \(\text{\text{C-H}}\) bond \((86 \text{ kcal})\).

- **initiation**

\[
\begin{align*}
\text{C}_6\text{H}_5\text{C} & + \text{R} \cdot \quad \rightarrow \quad \text{C}_6\text{H}_5\text{C} \cdot \quad + \quad \text{R} \quad \text{H}
\end{align*}
\]

The benzenecarbonyl radical, \(\text{\text{C}_6\text{H}_5\text{C} \cdot}\), then propagates a chain reaction.

- **propagation**

\[
\begin{align*}
\text{C}_6\text{H}_5\text{C} & \quad + \quad \text{O}_2 \quad \rightarrow \quad \text{C}_6\text{H}_5\text{C} \quad \text{O} \quad \text{O} \cdot \\
\text{C}_6\text{H}_5\text{C} & \quad + \quad \text{C}_6\text{H}_5\text{C} \quad \rightarrow \quad \text{C}_6\text{H}_5\text{C} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{H} + \quad \text{C}_6\text{H}_5\text{C} \cdot \\
\text{peroxybenzenecarboxylic acid}
\end{align*}
\]

The peroxy acid formed then reacts with benzenecarbaldehyde to give two molecules of carboxylic acid:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{C} & \quad + \quad \text{C}_6\text{H}_5\text{C} \quad \rightarrow \quad 2\text{C}_6\text{H}_5\text{C} \quad \text{O} \quad \text{O} \quad \text{H} \quad \text{(16-8)}
\end{align*}
\]

The oxidation of benzenecarbaldehyde with peroxybenzenecarboxylic acid (Equation 16-8) is an example of a reaction of wide applicability in which aldehydes are oxidized to carboxylic acids, and ketones are oxidized to esters.
The reaction, which is known as the **Baeyer-Villiger oxidation**, has synthetic utility, particularly for the oxidation of ketones to esters because ketones normally are difficult to oxidize without degrading the structure to smaller fragments. Two examples of the Baeyer-Villiger reaction follow:

The mechanism of the Baeyer-Villiger oxidation has been studied extensively and is of interest because it involves a rearrangement step in which a substituent group \( \text{R} \) moves from carbon to oxygen. The reaction sequence is shown in Equations 16-9 through 16-11:

In the first step, Equation 16-9, the peroxy acid adds to the carbonyl group. The adduct has several oxygen atoms on which protons can reside, and there will be rapid shifts of protons between these oxygens. However, at some stage the structure will be appropriate to allow elimination of a molecule of carboxylic acid, \( \text{R'C}O_2H \), Equation 16-10. The resulting intermediate has an electron-deficient oxygen atom with only six valence electrons. As with carbocations and borane complexes (Sections 8-9B, 15-5E, 11-6E, and 16-9D,G), a neighboring \( \text{R} \) group can move over with its bonding electron-pair to the electron-deficient (oxygen) atom, Equation 16-11. You will notice that for aldehydes, the aldehyde hydrogen migrates in preference to the alkyl or aryl group. In the other examples given, a cycloalkyl migrates in preference to a methyl group, and aryl in preference to methyl.

**Contributors**