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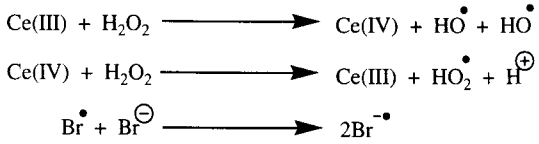
Figure 2.3 *Polarization of hydrogen peroxide.*

philic and nucleophilic properties. The electrophilic character arises from the fact that the O—O bond is easily polarized (Figure 2.3).

Undissociated hydrogen peroxide behaves, to some extent, as a nucleophile, being about 10^4 times more nucleophilic than water. For example, hydrogen



peroxide readily adds to carbonyl bonds giving rise to hydroxyhydroperoxides (peracetals and perketals). Such compounds are often used as polymerization initiators on account of their radical decomposition at moderate temperatures (O—O bond homolysis). Neutral hydrogen peroxide can also react with activated acyl compounds such as anhydrides to give peroxyacids.

The perhydroxyl anion, HO_2^-, is a powerful nucleophile (see Chapter 3) and will attack substrates such as electron-deficient olefins (*e.g.* α,β-unsaturated ketones) and aldehydes.

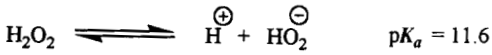


Figure 2.4 *Dissociation of hydrogen peroxide under alkaline pH.*

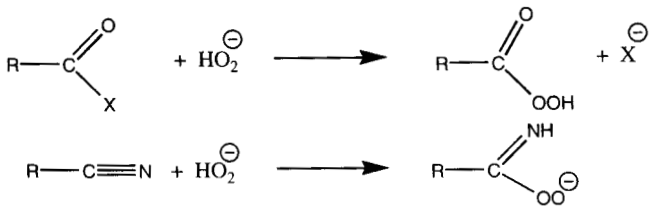


Figure 2.5 *Generation of more powerful oxidants (use of perhydroxyl anion).*

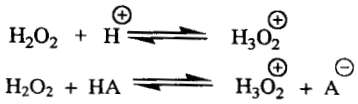


Figure 2.6 *Action of strongly acidic conditions on hydrogen peroxide.*