

Reactive Radicals in Advanced Oxidation Processes: Rate Constants, Reduction Potentials, Mechanisms

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In advanced oxidation processes (AOP) reactive radicals induce the destruction of organic contaminants. Of these intermediates the strong oxidizing hydroxyl radicals ($\bullet\text{OH}$) are of primary importance. They react with most organic contaminants with rate constants between 10^8 and $10^{10} \text{ M}^{-1} \text{ s}^{-1}$. These reactions are controlled by both, diffusion and chemical reactivity. When the molecule contains double bond(s) (aromatic ring(s)) the basic reaction is radical addition. $\bullet\text{OH}$ reacts with aliphatic chains in H-abstraction reaction. When the HCO_3^- concentration is high, $\bullet\text{OH}$ transforms to the milder oxidant carbonate radical anion ($\text{CO}_3^{\bullet-}$). $\text{CO}_3^{\bullet-}$ reacts in direct oxidation by picking up an electron from the partner. These reactions are highly selective, the rate constants vary between 10^2 and $10^9 \text{ M}^{-1} \text{ s}^{-1}$. They are high when the attacked molecule has part(s) with increased electron density, such as aromatic rings with electron donating substituent (OH , O^-), amino groups, sulfur atoms. $\text{CO}_3^{\bullet-}$ reacts with aliphatic compounds in H-abstraction. The rate constant of $\bullet\text{OH}$ reaction with Cl^- is high, $4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. When the Cl^- concentration is above 0.1 mM, a considerable fraction of $\bullet\text{OH}$ reacts with Cl^- . The reaction below pH 6 leads to formation of dichloride radical anion ($\text{Cl}_2^{\bullet-}$) which is also a moderately strong oxidant reacting in similar way as $\text{CO}_3^{\bullet-}$.

In some AOPs (VUV photolysis, radiolysis) the reactions of the reductive hydrogen atom ($\text{H}\bullet$) and hydrated electron ($\text{e}_{\text{aq}}^{\bullet-}$) also contribute to pollutant degradation. $\text{H}\bullet$ reactions are similar in all aspects to $\bullet\text{OH}$ reactions, but the rate constants are 5-times smaller. $\text{e}_{\text{aq}}^{\bullet-}$ adds to parts of molecules which can accommodate extra electron (e.g., conjugated system), the reaction is followed by protonation.

The sulfate radical anion ($\text{SO}_4^{\bullet-}$) based AOP is yet under development. $\text{SO}_4^{\bullet-}$ is stronger oxidant as $\bullet\text{OH}$, it mainly reacts in direct oxidation. These reactions show some selectivity, the highest rate constants approach the diffusion controlled limit. $\text{SO}_4^{\bullet-}$ reacts with high rate constants with Cl^- limiting the applicability of this AOP.

In reactions of the mentioned radicals with organic molecules, carbon-centred radicals form. The reactions of carbon-centred radicals with dissolved oxygen (DO) basically determine the oxidation rate. Peroxy radicals formed in reactions of aliphatic carbon-centred radicals may transform to peroxides and hydroperoxides. Aromatic carbon-centred radicals (cyclohexadienyl radicals) react with DO reversibly; the ring degradation takes place from the peroxy radicals. The carbon-centred radicals in uni-, or bi-molecular processes may transform to oxygen or nitrogen centred radicals. These intermediates (e.g., phenoxy or anilino radicals) do not react with DO and, therefore, the degradation rate is low. The carbon-centred radical formed in reaction of a one-electron oxidizing radical undergoes a second oxidation when it reacts with DO. This reaction may be followed by further oxidations starting from the peroxy radical, or from the peroxide/hydroperoxide products. These reactions increase the degradation efficiency: the one-electron oxidants induce 2–4 electron oxidations.