

<https://doi.org/10.70200/RX202401034H>

CO₃^{•-}, THE RADICAL THAT CONNECTS PEROXYNITRITE AND FENTON CHEMISTRY

Willem H Koppenol^{1*}

^{1*}*Professor Emeritus, Swiss Federal Institute of Technology Zürich, Zürich, Switzerland,*
koppenol@inorg.chem.ethz.ch

Oxidative biochemistry centered about 35 years ago on the one-electron reduction of H₂O₂ by Fe²⁺, the Fenton reaction, to yield HO[•] and a Fe(III)-complex. The discovery that NO[•] is formed *in vivo* and that it reacts with O₂^{•-} at a diffusion-controlled rate led to ONOO⁻ as an additional oxidant. The rate constant of the Fenton reaction is 53 M⁻¹s⁻¹ up to about pH 4, but above it the rate constant increases linearly with pH. This acceleration of the Fenton reaction led to the hypothesis that above pH 5 formation of FeO²⁺ predominates. Thermodynamically, this species is comparable to HO[•] as an oxidant. HCO₃⁻ accelerates the reaction even more, and convincing evidence has been presented that the complex of Fe²⁺ with CO₃²⁻ reacts with H₂O₂ to form CO₃^{•-} and a Fe(III)-complex, conceivably *via* FeO²⁺ as an intermediate. The rapid reaction of ONOO⁻ with CO₂ ($k > 10^7$ M⁻¹s⁻¹) leads to ONOOCO₂⁻ that, depending on the CO₂ concentration, yields varying amounts of NO₂[•] and CO₃^{•-}. These two oxidizing radicals together nitrate aromatic residues. Compared to 35 years ago, oxidative biochemistry is no longer concerned with the indiscriminate oxidations and additions of HO[•], but with the more selective reactions of CO₃^{•-} and NO₂[•].