$CO_3^{\bullet-}$, THE RADICAL THAT CONNECTS PEROXYNITRITE AND FENTON CHEMISTRY

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Oxidative biochemistry centered about 35 years ago on the one-electron reduction of H_2O_2 by Fe^{2+}, the Fenton reaction, to yield $HO^\bullet$ and a Fe(III)-complex. The discovery that $NO^\bullet$ is formed *in vivo* and that it reacts with $O_2^{\bullet-}$ at a diffusion-controlled rate led to $ONOO^-$ as an additional oxidant. The rate constant of the Fenton reaction is 53 $M^{-1}s^{-1}$ 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 FeO^{2+} predominates. Thermodynamically, this species is comparable to $HO^\bullet$ as an oxidant. HCO_3^- accelerates the reaction even more, and convincing evidence has been presented that the complex of Fe^{2+} with CO_3^{2-} reacts with H_2O_2 to form $CO_3^{\bullet-}$ and a Fe(III)-complex, conceivably *via* FeO^{2+} as an intermediate. The rapid reaction of $ONOO^-$ with CO_2 ($k > 10^7$ $M^{-1}s^{-1}$) leads to $ONOOCO_2^-$ that, depending on the CO_2 concentration, yields varying amounts of $NO_2^\bullet$ and $CO_3^{\bullet-}$. 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 $HO^\bullet$, but with the more selective reactions of $CO_3^{\bullet-}$ and $NO_2^\bullet$.