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Two tyrosyl radicals stabilize high oxidation states in cytochrome *c* oxidase for efficient energy conservation and proton translocation¹

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The reaction of hydrogen peroxide (H_2O_2) with oxidized bovine cytochrome *c* oxidase (bCcO) was studied by electron paramagnetic resonance (EPR) to determine the properties of radical intermediates. Two distinct radicals with widths of 12 and 46 G are directly observed by X-band CW-EPR in the reaction of bCcO with H_2O_2 at pH 6 and pH 8. High-frequency EPR (D-band) provides assignments to tyrosine for both radicals based on well-resolved *g*-tensors. The 46 G wide radical has extensive hyperfine structure and can be fit with parameters consistent with Y129. However, the 12 G wide radical has minimal hyperfine structure and can be fit using parameters unique to the post-translationally modified Y244 in CcO. The results are supported by mixed quantum mechanics and molecular mechanics calculations. This study reports spectroscopic evidence of a radical formed on the modified tyrosine in CcO and resolves the much debated controversy of whether the wide radical seen at low pH in the bovine system is a tyrosine or tryptophan. A model is presented showing how radical formation and migration may play an essential role in proton translocation. This work was done in collaboration with Michelle A. Yu, Tsuyoshi Egawa, Syun-Ru Yeh and Gary J. Gerfen from Albert Einstein College of Medicine; Kyoko Shinzawa-Itoh and Shinya Yoshikawa from the University of Hyogo; and Victor Guallar from the Barcelona Supercomputing Center.

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