

P012 FTIR detection of carboxyl groups in bovine heart cytochrome *c* oxidase.

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FTIR spectroscopic studies of bovine heart cytochrome *c* oxidase (CcO) have revealed carboxyl group changes upon redox change of the Cu_A-heme *a* moiety and on CO dissociation from heme *a*₃. In both cases, the changes are more complex than in bacterial CcOs in that they involve more than one carboxyl group. For all CcOs, it is thought that Glu242, a conserved residue crucial for the interhaem electron transfer, is involved. In the case of bovine CcO, other contributions could come from Asp51 and Asp91, residues that may be involved in different proton transfer pathways. To investigate this further, FTIR difference spectra were recorded in the presence of metal and/or cation bound to CcO. The binding site of Ca²⁺/Na⁺ is very close to Asp51 and could affect any redox- or ligand-linked structural changes that it might undergo. Recent crystallographic studies indicate that the binding of Zn²⁺/Cd²⁺ to CcO acts at a site in the D-channel close to Asp91 and could well inhibit any redox-dependent protonation changes that it might undergo. The effects of these metals on the redox- and CO photolysis-induced difference spectra will be reported and the implications of the data for linkage of specific carboxyl groups to redox and ligand changes will be assessed.