The reaction between *c*-type cytochromes and Fe(II): Ligand effects and mechanisms

YING WANG, XIAOMIN LI, TONGXU LIU*, FANGBAI LI*

Guangdong Institute of Eco-Environmental and Soil Sciences, Guangzhou, P. R. China 510650.
txliu@soil.gd.cn; cefbli@soil.gd.cn

Cytochrome *c* (*c*-Cyts) might play an important role in microbial Fe(II)-oxidizing process. In this study, the equine *c*-Cyts containing 1 heme, which has similar structure with the *c*-Cyts of Fe(II)-oxidizing microorganisms, was used as a model protein, to study the effect of different organic ligands on the rapid redox reaction between Fe(II) and *c*-Cyts with the stopped-flow device, and the order of rate constants were obtained as follows: EDTA> citric acid > NTA > malonic acid > salicylic acid > glycine amino acid > acetate ≈ glutamic acid ≈ ethidene diamine ≈ CK. The results of correlation analysis between the complex constants of Fe(II)-ligands and the rate constants of *c*-Cyts reduction show that the higher complex constants of Fe(II)-ligand, the more contents of Fe(II)-ligand species, the higher reaction rate constants. Further analysis according to the ligand structure indicates that the constants of reaction rate is highly positive related with the complex constants of Fe(II)-ligand for the Group 1 ligands (EDTA, NTA and ethidene diamine; r = 0.995) and Group 2 ligands (citric acid, malonic acid and acetate; r = 0.999), which both have similar structures in each group. However, not any correlation of reaction rate constants with the complex constants observed for all the ligands with different structures from different groups. In addition, the results of midpoint potentials of all Fe(II)-ligands obtained through the cyclic voltammetry (CV) test in a potential range -0.8 V to 0.8 V (vs. SHE) with a scan rate of 50 $mV \cdot s^{-1}$, show that the redox potentials of Fe(II) complexes with similar structures shows the highly positive correlation (r = 0.996 for Group 1 ligands, r = 0.986 for Group 2 ligands) with the rate constants of the reaction between Fe(II)-ligand and *c*-Cyts. Due to the calculation formula of the reaction active energy, the above results indicate that the structure of Fe(II)-ligand and the reorganization energy of electron-transfer reaction may contribute more significantly than the Gibbs free energy (ΔG) of electron-transfer reaction to the reaction kinetics of Fe(II)-ligand and *c*-Cyts.

This work was funded by the National Natural Science Foundations of China (41601240, 41471216 and 41522105).