On the electron transfer properties of blue copper proteins

Mats H. M. Olsson and Arieh Warshel

University of Southern California
Department of Chemistry, SGM 418
3620 McClintock ave.
Los Angeles, CA, 90089

The blue copper proteins are a group of electron transfer proteins that are characterised by a number of unusual properties, e.g. a bright blue colour, a narrow hyperfine splitting in the electronic spin resonance spectra, and a high reduction potential. Moreover, crystal structures of the oxidised form of these proteins show a ligand structure distinct from what is normally observed for small inorganic complexes: the copper ion is bound to the protein in an approximate trigonal plane formed by a cysteine thiolate group and two histidine nitrogen atoms. The coordination sphere in most blue copper proteins is completed by one or two axial ligands, typically a methionine tioether group. Such a geometry is similar to what can be expected for Cu(I) commplexes. Naturally, this is a functional advantage for an electron transfer protein; if the copper centre has similar structure for the two oxidation states, the reorganisation energy will be low and the rate of electron transfer will be high. Further, the blue copper proteins span a wide range of reduction potentials (200 - 1000 mV).

These unusual properties of the blue copper proteins have traditionally been explained by protein strain. However, protein strain is an elusive property that is difficult to examine with todays experimental approaches. Theoretical investigations, on the other hand, have been limited to small model complexes mimicing the active site of the protein, thereby missing an essential part of the protein function. Here, we present a detailed investigation of the electron transfer properties of plastocyanin and rusticyanin, two blue copper proteins with an identical active site, but drastically different reduction potential (375 and 680 mV respectively). For this purpose, we have, in addition to classical simmulation techniques, used the frozen DFT approach (FDFT) that enables us to treat large parts of the protein quantum mechanically, while retaining proper configuration sampling.

Reorganisation energy

The reorganisation energy is one of the important parameters governing the electron transfer rate of a protein and should, in general, be minised for an efficient transfer. Though we have concentrated our investigation of the reorganisation energy on plastocyanin since it is experimentally better characterised, we have investigated both proteins with several different methods and find that they are of similar magnitude. Our calculations indicate that the reorganisation energy of plastocyanin is about 20 kCal/mole, which is similar to experimental estimates. However, the uncertanties both in calculated and experimental values are probably not insignificant, thus, it is more instructive to compare the protein reorganisation with that of the protein active site in water. It is found that the protein lowers the over-all reorganisation energy to between 1/2 and 1/4 of that in water. Thus, one of the main mechanisms of the protein is to exclude water from the active site.

Reduction Potential

For calculating the reduction potential, it is important to have a correct reference system to compare with. It comes natural to choose the protein active site as such a reference since water is the solvent for most reactions both in and outside the cell, further, it is instructive when discussing the "catalytic effect" of proteins. However, since it has turned out to be difficult to synthesize such a complex and there is no reliable experimental data available, we have focused on reproducing the difference in reduction potential between plastocyanin and rusticyanin, which is experimentally well known.

Table I

Reduction potential (mV)

	Plastocyanin	Rusticyanin	Diff.
Experiment	375	680	305
Calculated	327	619	292

We have calculated total reorganisation energies and reduction potentials of both plastocyanin and rustycyanin and reproduced the experimental values, where available. The difference between these two proteins can be explained by the electrostatic effect from the environment, thus, showing that mechanical strain is of minor importance for the fuction of blue copper proteins.

ACKNOWLEDGEMENTS

This work was supported by The Swedish Research Council.

REFERENCES

1. R. H. Holm, P. Kennepohl and E. I. Solomon, Chem. Rev., **96**, 2239 (1996)

2. J. A. Guckert, M. D. Lowery and E. I. Solomon, J. Am. Chem. Soc., **117**, 2817 (1995).

3. H. B. Gray, B. G. Malmstrom and R. J. P. Williams, J. Biol. Inorg. Chem., **5** (2000).

4. B. L. Vallee and R. J. P. Williams, Proc. Nat. Acad. Sci., **59**, 498 (1968).

5. U. Ryde, M. H. M. Olsson, B. O. Roos, J. O. A. De Kerpel and K. Pierloot, J. Biol. Inorg. Chem., **5**, 565 (2000).

ECS Electronic Meeting Abstract Form

Running #... Session ...

Symposium Information

Meeting:	...
Code:	AE2
Division:	
Title:	
Organizers:	

Other Papers in Symposia:

Meeting Abstracts Volume 96-1

Title: On the electron transfer properties of blue copper proteins

Presenting Author:
Olsson, Mats H. M.
University of Southern California

Society Member: Yes ☐ No ☒

Complete Author List:

Mats H. M. Olsson
Phone: 213-740-7671
Fax: 213-740-2701
E-Mail: molsson@usc.edu

Arieh Warshel
Phone: 213-740-4114
Fax: 213-740-2701
E-Mail: warshel@usc.edu

University of Southern California
Department of Chemistry, SGM 418
3620 McClintock ave.
Los Angeles, CA, 90089

Oral preferred ☒ Poster preferred ☐

Audio/Visual Equipment:

- ☐ 35mm Slides
- ☐ Overhead projector
- ☐ Other