# Catalytic properties, EPR characteristics and reversible inactivation by cyanide of formylmethanofuran dehydrogenase, a molybdenum or tungsten iron-sulfur protein from methanogenic archaea

Bertram, P.A.; Schmitz, R.A.; Karrasch, M.; Hochheimer, A.; Albracht, S.P.J.; Thauer, R.K.

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## P06 CATALYTIC PROPERTIES, EPR CHARACTERISTICS AND REVERSIBLE INACTIVATION BY CYANIDE OF FORMYLMETHANOFURAN DEHYDROGENASE, A MOLYBDENUM OR TUNGSTEN IRON-SULFUR PROTEIN FROM METHANOGENIC ARCHAEA.

**P.A. Bertram,[a] R.A. Schmitz,[a] M. Karrasch,[a] A. Hochheimer,[a] S.P.J. Albracht,[b] R.K. Thauer.[a]**

*[a]Max-Planck-Institut für Terrestrische Mikrobiologie and Laboratorium für Mikrobiologie, FB Biologie, Philipps-Universität, Karl-von-Frisch-Str., 35043 Marburg, Germany. [b]E.C. Slater Institute for Biochemical Research, University of Amsterdam, Plantage Muidergracht 12, NL-1018 TV Amsterdam, The Netherlands.*

Formylmethanofuran dehydrogenases, which are found in methanogenic Archaea, are molybdenum or tungsten iron-sulfur proteins that contain a pterin cofactor [1]. We report here on differences in catalytic and EPR properties and susceptibility to inactivation by cyanide of the enzymes from *Methanosarcina barkeri*, *Methanobacterium thermoautotrophicum* and *Methanobacterium wolfei* [2].

The Mo formylmethanofuran dehydrogenases displayed at 77 K two rhombic EPR signals, designated $FMD_{red}$ and $FMD_{ox}$, both derived from Mo as evidenced by isotopic substitution with $^{97}Mo$. The $FMD_{red}$ signal was only exhibited by the reduced active enzyme and was lost upon enzyme oxidation. The $FMD_{ox}$ signal was displayed by an inactive form and was not quenched by oxygen. The W isoenzymes were EPR silent at 77 K.

The Mo formylmethanofuran dehydrogenases were found to be inactivated by cyanide and reactivated by sulfide, both with concurrent changes in the Mo derived EPR signals. In contrast, the W isoenzymes were not inactivated by cyanide treatment.

At temperatures between 77 K and 14 K the Mo isoenzyme from *M. wolfei* displayed distinct EPR signals that were ascribed to the presence of two [2Fe-2S] centers and at least one [4Fe-4S] center.

Evidence is presented that the formylmethanofuran dehydrogenases belong to the group of molybdenum (tungsten) enzymes that catalyze the insertion of an oxygen atom derived from water into a C-H bond.

1. R.A. Schmitz, S.P.J. Albracht, and R.K. Thauer, *Eur. J. Biochem.*, 209, 1013 (1992).
2. P.A. Bertram, M. Karrasch, R.A. Schmitz, R. Böcher, S.P.J. Albracht, and R.K. Thauer, *Eur. J. Biochem.*, 220, 477 (1994).