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Recent Advances in the Understanding of Inorganic/Bioinorganic Reaction Mechanisms

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The elucidation of inorganic/bioinorganic reaction mechanisms has in recent years benefited from the application of high pressure thermodynamic and kinetic measurements, as well as low-temperature rapid-scan techniques. The high pressure studies have enabled us to construct volume profiles for typical solvent exchange processes, and the activation of small molecules by transition metal complexes, from which detailed mechanistic insight could be obtained [1-3].

The low-temperature rapid-scan techniques were employed to study the activation of peroxides by model complexes for P450 and related porphyrin systems. It is our goal to contribute towards the mechanistic understanding of the different iron-porphyrin intermediates that participate in catalytic oxidation reactions of substrates by different oxidants. Of special interest is the activation of hydrogen peroxide, organic peroxides and peroxy acids by functional model iron-porphyrins. Low-temperature rapid-scan techniques were used to characterize the intermediates that participate in the catalytic cycles and to study their kinetic behaviour [4-7]. The obtained data allowed us to distinguish between the reactivity of Fe(III) peroxo (Cpd 0), (Porphyrinⁿ⁺)FeIV=O (Cpd I) and (Porphyrin)FeIV=O (Cpd II) species in epoxidation, sulfoxidation, hydrogen abstraction and hydride transfer reactions[8, 9]. Detailed mechanistic insight will be presented.

- [1] C.D. Hubbard, R. van Eldik, in *Physical Inorganic Chemistry. Principles, Methods and Models*, A. Bakac (Ed.), Wiley, (2010), p. 269-365.
- [2] I. Ivanovic-Burmazovic, R. van Eldik, *Perspective article in Dalton Trans.* (2008), p. 5259-75.
- [3] R. van Eldik, C.D. Hubbard, *Coord. Chem. Rev.* **254**, 297-308 (2010).
- [4] N. Hessenauer-Ilicheva, A. Franke, D. Meyer, W.-D. Woggon, R. van Eldik, *J. Am. Chem. Soc.* **129**, 12473-79 (2007).
- [5] A. Franke, M. Wolak, R. van Eldik, *Chem. Eur. J.***15**, 10182-98 (2009).
- [6] N. Hessenauer-Ilicheva, A. Franke, D. Meyer, W.-D. Woggon, R. van Eldik, *Chem. Eur. J.***15**, 2941-59 (2009).
- [7] N. Hessenauer-Ilicheva, A. Franke, M. Wolak, T Higuchi, R. van Eldik, *Chem. Eur. J.***15**, 12447-59 (2009).

- [8] C. Fertinger, A. Franke, R. van Eldik, *Angew. Chem. Int. Ed.***47**, 5238-42 (2008).
- [9] C. Fertinger, N. Hessenauer-Ilicheva, A. Franke, R. van Eldik, *Chem. Eur. J.***15**, 13435-40 (2009).