are described. The second methods based chapter is Chapter 7 (Dey and Dey) on experimental based techniques, such as magnetic circular dichroism, X-ray absorption spectroscopy and extended X-ray absorption fine structure. Both methods based chapters discuss non-heme iron dioxygenases as well as biomimetic model complexes. A detailed and thorough review on non-heme iron biomimetics is found in Chapter 6 (Costas and coworkers).

The second section of this book describes heme based monoxygenases and dioxygenases. The most common and most thoroughly studied of these are the cytochrome P450 enzymes and Munro and coworkers give a detailed biochemical overview of their structure, mechanism and function (Chapter 8). A computational perspective on the mechanism of substrate activation, as it, for instance, appears in drug metabolizing reactions, is given in Chapter 9 (Kumar), which also details the concept of two-state-reactivity that drives the reaction mechanisms. The cytochromes P450 are highly versatile and hence many bioengineering studies have taken place to make them more biotechnologically relevant. Key studies in this field are reviewed by Mazumdar and coworkers in Chapter 10. Further computational advances have led to the development of quantum mechanics/molecular mechanics techniques for the studies of large (bio)chemical systems. Mulholland and coworkers review the method and describe recent applications in the field of cytochrome P450 chemistry in Chapter 11. The final chapter (Chapter 12, Mowat and coworkers) is focused on the biochemical structure, function and mechanism of heme based dioxygenases, including tryptophan dioxygenases and indoleamine dioxygenases.

Finally, we (the editors) thank all the authors for their contributions and prompt submission of their manuscripts. We are very grateful for the valuable time spent by the authors to create this detailed overview of recent highlights in a fast-moving field of research.

Sam P. de Visser and Devesh Kumar

Preface

Heme and non-heme based monoxygenases and dioxygenases are fascinating enzymes that are found in all forms of life. They are involved in vital biochemical processes and are extremely versatile. As such there is huge interest in commercial applications of these systems in biotechnology. Despite the broad interest and applications, though, their structure, mechanism and functions are still not fully understood. However, in recent years a combination of experimental and computational studies has led to significant breakthroughs in the field. In particular, it is now known that many heme and non-heme enzymes use molecular oxygen on an iron center and synthesize an iron(IV)-oxo active species during their catalytic cycle. This key intermediate is involved in oxygen atom transfer reactions to a substrate, hence the heme and non-heme iron based mono- and dioxygenases catalyze aliphatic hydroxylation as well as epoxidation, desaturation and heteroatom oxidations.

This book gives an overview of recent advances in heme and non-heme iron(IV)-oxo chemistry as well as biomimetic analogues. The first five chapters are specifically devoted to the non-heme iron containing dioxygenases, where Chapter 1 (de Visser) gives a general overview on the various mechanisms of the different types of dioxygenases and how computational research assisted in the elucidation of the reaction mechanisms. Chapter 2 (Bugg) then continues with an overview of, mainly, Rieske-type (intradiol and extradiol) dioxygenases, their function and mechanism. The third chapter (Proshlyakov and Hausinger) is completely dedicated to studies performed on taurine/α-ketoglutarate dioxygenases, which are a biological system that essentially has functioned as a template for non-heme iron dioxygenases in general. Chapter 4 (Borowski and Siegbahn) describes detailed computational studies of the Stockholm and Kraków groups on various non-heme iron-containing enzymes and how these studies have further guided experiment. Two chapters in this volume are dedicated to the description of often-used methods in the field: the first is Chapter 5 (Neese and coworkers), where recently developed computational models for the calculation of spectroscopic parameters of iron-based systems

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