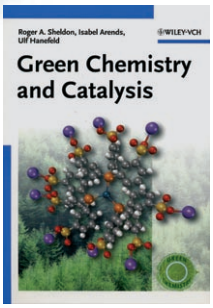
Green Chemistry and Catalysis



By *Roger A. Sheldon, Isabel Arends* and *Ulf Hanefeld*. Wiley-VCH, Weinheim 2007. 434 pp., hardcover € 139.00.—ISBN 978-3-527-30715-9

"Ein gutes Buch mit einem schlechten Titel, und schnell sind alle Hoffnungen zerstoben!" (A good book with a bad title, and all hope is quickly lost) Carola Stern in *Doppelleben* (2004)

While reading this excellent and important book, a question that unavoidably comes to mind is whether Carola Stern's theory, which has been adopted as a motto, applies also to specialist books such as this, and whether there are other good and accurate books on chemical subjects that have incorrect titles. That question will be answered at the end of this review.

In *Green Chemistry and Catalysis*, Roger Sheldon, the renowned veteran of catalysis, and his two younger colleagues Isabel Arends and Ulf Hanefeld, have written a book about the state of modern catalytic reactions from the viewpoints of sustainable chemistry, safe operation, and (where possible) the use of renewable raw materials. In their preface, the authors introduce the subject by concentrating on those aspects in a rational way. In addition, their colleague Poliakoff contributes a foreword in which he sees added value in the book, since its two aims—to discuss new processes, *and also* to do that from a green viewpoint—mean that, in effect, the reader gets two books for the price of one.

Poliakoff's comment is partly justified, as the book begins with a digression on "Green Catalysis and Chemistry" (Chapter 1), in which the fundamental beliefs of "green chemistry" are stated emphatically, also for unbelievers and renegades (and, as always in disputes between different faiths, in a tone of complete conviction and absolute truth). The chapter outlines the basic procedure for evaluating alternative processes by using the concepts of the "*E* factor" or Trost's atom-economy principle. Not surprisingly, of course, Sheldon's *E* factor is presented as the preferred method, because of its general applicability, even for different types of products that differ widely in their complexity (and their demands on the environment), compared with the oversimplified and greatly overrated atom-economy method. Other topics discussed in Chapter 1 include the role of solvents, ways of avoiding the release of waste products, renewable feedstocks, and "risky reagents" such as phosgene, HCl, chlorine, and formaldehyde. It also commends "white biotechnology" and explains the advantages of enantioselective catalysis.

Chapter 2 deals with solid acids and bases, including zeolites, hydrotalcite, clays, and hetero-polyacids. Catalytic reactions are described in the chapters that follow. Chapter 2 is the only one in which the material is arranged according to the different catalysts rather than the reactions. Chapters 3–6 describe in detail the current state of knowledge of the science (and partly also of the technology) of heterogeneous and homogeneous catalysis, and also of biocatalysis, in particular for the reactions of oxidation, C–C bond formation, and hydrolysis, with many interesting and well-chosen examples.

Chapter 7 is concerned with new reaction media (supercritical fluids such as $scCO_2$, ionic liquids) and with the new two-phase and multiphase processes based on water, fluorous liquids, and combinations of immiscible organic solvents. Thermomorphic, thermoregulated, and thermoresponsive variants are mentioned. However, some new and highly topical methods such as those based on "near-critical water" and Sharpless reactions or catalyses carried out "on water" are not covered. This chapter also discusses some important catalytic reactions that were not covered in the earlier chapters, such as hydrogenation, carbonylation, and hydroformylation, within the context of the technology for carrying out these reactions in new media.

Chapter 8 focuses on chemicals derived from renewable raw materials. As well as the age-old and almost prehistoric processes for the production of ethanol, acetic acid, fats, and oils, the chapter discusses new routes to lactic acid, 1,3-propandiol, pantothenic acid, and carbohydrate derivatives. This chapter, in its concentration on renewable and "green" feedstocks and biomass, is the one that most closely follows the "politically correct" aims of "green chemistry". Although the authors concede that there are "many shades of green", they do not follow the road consistently to its conclusion, since the most important criterion for a truly renewable chemistry and catalysis—the overall life-cycle assessment of each new process or proposed new process—is not brought into the discussion, or even mentioned!

In support of the theory of "green chemistry", Chapter 9 describes possibilities for process integration and process intensification, for separation of racemates, for asymmetric transformations, and for catalytic processes in the form of cascades. Lastly, Chapter 10 celebrates green chemistry as a "Road to Sustainability", and announces that "The Medium is the Message", phrases that are about as ambiguous (and misleading) as is possible.

Sheldon's exercise in concentrated presentation of well-chosen examples, which are of great pedagogical value, is followed by a clear presentation of the factual material. The literature coverage up to 2006 for the examples described is fairly comprehensive, and, taken together with the discussions in the text, gives a very good, up-to-date, and complete picture of the subject that the authors describe as "green".

A second edition of the work (which will certainly become necessary in the future) could incorporate improvements to take the following points into account. Although the subject index

also serves as a name index to some extent (as in the examples of the Baeyer–Villiger pair, Chauvin, Ostwald, and firms such as AstraZeneca, Mitsubishi, and Rhodia), some important developments in the area of catalysis that are described in the text, such as the Ruhrchemie/Rhône–Poulenc two-phase catalytic process, do not appear in the index. In Chapter 8, the evaluation of processes based on renewable raw materials should take into account the overall life-cycle assessment; for example, the evaluation of biodiesel is quite different when one takes into account the enormous quantities of fertilizer that must be applied to grow the crops (without which the production of biodiesel would not be feasible).

Now I return to Chapter 1, and to the still unanswered question at the beginning of this review. Chapter 1 is important, and the information in it is presented in a well-balanced way, with the arguments carefully set out in the context of a sound theory of "green chemistry". But this theory is presented with the benefit of hindsight, relying on and usurping all the progress achieved by chemists before 1990 (the year in which green chemistry was born, according to Poliakoff in his foreword), in the areas of selectivity, reduction of side-products and wastes, mild reaction conditions, avoidance of "risky reagents", better energy economy, fewer reaction stages, etc. Thus, it discredits the commendable efforts of whole generations of chemists (or, at least, regards their work as having been based on a "non-green", and therefore immature and disreputable, theory). In fact, however, the worthwhile aims and dedication of chemists of the past, without any kind of ideology, led to beneficial results that were certainly "green", such as higher yields and better selectivity, the introduction of catalytic processes wherever possible, avoidance of the need for solvents, milder reaction conditions, and the use of indigenous raw materials where possible—and all this before 1990! Hydroformylation is a classic example of this: the 30 % increase in efficiency achieved during the last 30 years did not take place under the label "green", but in the context of the general push to improve processes and catalysts. The motivation for the introduction of ligand-modified catalysts and of a two-phase process had nothing to do with any green ideology. One does not need to perform a calculation according to the rules of "atom economy" to recognize that the 99 % yield normally achieved nowadays with this addition reaction is better than the 66 % that was typically obtained 30 years ago!

On page XI of the book, Sheldon, Arends, and Hanefeld define green chemistry as follows: "Green chemistry efficiently utilizes (renewable) raw materials, eliminates waste, and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products". This definition is a description of what generations of chemists have been doing to the best of their ability, without thinking "green"—therefore, why must it be called "green", if the prefix "green" adds nothing to our understanding? Thus, the question posed at the beginning of this review can be answered very easily: this book by Sheldon, Arends, and Hanefeld is a useful book that can certainly be recommended, but its title does not fit the content!

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DOI: 10.1002/anie.200785509

