

# 国外化学名著系列

(影印版)6

〔荷〕 Piet W.N.M. van Leeuwen

## Homogeneous Catalysis

Understanding the Art

## 均相催化

——理解艺术



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## Preface

Homogeneous catalysis using transition metal complexes is an area of research that has grown enormously in recent years. Many amazing catalytic discoveries have been reported by researchers both in industry and in academia. Reactions that were thought to be well understood and optimised have now been revolutionized with completely new catalysts and unprecedented product selectivities. Our knowledge in this area has increased accordingly, but much of this information is still only to be found in the original literature. While the field of homogeneous catalysis is becoming more and more important to organic chemists, industrial chemists, and academia, until now there has been no book available that gives real insight in the many new and old reactions of importance. This book aims to provide a balanced overview of the vibrant and growing field of homogeneous catalysis to chemists trained in different disciplines, and to graduate students who take catalysis as a main or secondary subject.

The book presents a review of sixteen important topics in modern homogeneous catalysis. While the focus is on concepts, many key industrial processes and applications that are important in the laboratory synthesis of organic chemicals are used as real world examples. After an introduction to the field, the elementary steps needed for an understanding of the mechanistic aspects of the various catalytic reactions have been described. Chapter 3 gives the basics of kinetics, thus stressing that kinetics, so often neglected, is actually a key part of the foundation of catalysis.

The approach in the catalysis chapters has been to introduce the key concepts and important examples, rather than to present a complete listing of catalysts, ligands, and processes, which would anyway be impossible within this single



volume. Readers requiring this level of depth and completeness on a given reaction are pointed (through references) toward many dedicated books that present the individual topics with all the details in a comprehensive way. The literature chosen is a very personal choice of what I thought crucial to the development of an understanding of a given reaction. A few chapters remain descriptive in the absence of better studies, but they have been included because of their importance, and in order to cover the full range of topics such as fine chemicals, bulk chemicals, polymers, high-tech polymers, pharmaceuticals, reaction types, etc. For a few reactions, I have included the process schemes, environmental concerns and safety aspects, in an attempt to encourage catalyst researchers to think about these topics at an early stage of their projects and communicate with chemical engineers, customers and the end-users.

Astonishment and awe signalled the early chapters of modern day science; a deeper understanding is not the end of this era of marvel and amazement, but simply the next exciting chapter.

## Acknowledgments

I gratefully acknowledge my indebtedness to many people for their input in this project. During many years my co-workers at Shell, the University of Amsterdam, and colleagues in many other places have contributed with their presentations, their observations, and discussions to my courses in “homogeneous catalysis”, which eventually condensed in this book. A book like this requires more than just the writing, as being read is the primary goal. The students in the course of spring 2003 in Amsterdam worked a lot on the drafts and they made many suggestions, more than I could follow up. I am indebted to Alessia Amore, David Dominguez, Tanja Eichelsheim, René den Heeten, Mark Kuil, Renske Lemmens, Tomasso Marcelli, Maayke Mars, Angelica Marson, Teresa Monzón, Erica Nöllen, and Fabrizio Ribaudo for their valuable contributions.

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*Amsterdam, December 2003, Piet van Leeuwen*

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## Chapter 1

# INTRODUCTION

*What it is all about*

### 1.1 Catalysis

Catalysis plays a key role in the industrial production of liquid fuels and bulk chemicals. More recently the producers of fine chemicals have started to utilise catalytic conversions in their processes. For oil processes heterogeneous catalysts are preferred with one exception, the alkylation reaction for which liquid acids are being used. For the conversion of petrochemicals both homogeneous and heterogeneous catalysts are used. The number of homogeneously catalysed processes has been steadily growing in the eighties and nineties. For fine chemicals a variety of sophisticated homogeneous catalysts is being used. In the laboratory a wide range of catalytic reactions has become indispensable.

The term catalysis was coined by Berzelius over 150 years ago when he had noticed changes in substances when they were brought in contact with small amounts of certain species called "ferments". Many years later in 1895 Ostwald came up with the definition that we use until today: *A catalyst is a substance that changes the rate of a chemical reaction without itself appearing into the products.* This means that according to Ostwald a catalyst can also slow down a reaction! The definition used today reads as follows: *A catalyst is a substance which increases the rate at which a chemical reaction approaches equilibrium without becoming itself permanently involved.*

The "catalyst" may be added to the reactants in a different form, the catalyst precursor, which has to be brought into an active form ("activated"). During the catalytic cycle the catalyst may be present in several intermediate forms when we look more closely at the molecular level. An active catalyst will pass a number of times through this cycle of states; in this sense the catalyst remains unaltered. The number of times that a catalyst goes through this cycle is the turnover number. The turnover number (TON) is the total number of substrate

molecules that a catalyst converts into product molecules. The turnover frequency (TOF) is the turnover number in a certain period of time. Substrates are present in larger amounts than the catalyst; when we report on catalytic reactions the ratio of substrate to catalyst is an important figure.

An inhibitor is a substance that retards a reaction. An inhibitor is also present in "catalytic" or sub-stoichiometric amounts. In a radical chain reaction an inhibitor may be a radical scavenger that interrupts the chain. In a metal catalysed reaction an inhibitor could be a substance that adsorbs onto the metal making it less active or blocking the site for substrate co-ordination. We also talk about a poison, a substance that stops the catalytic reaction. A poison may kill the catalyst. The catalyst dies, we say, after which it has to be regenerated wherever possible. We will often see the word co-catalyst, a substance that forms part of the catalyst itself or plays another role somewhere in the catalytic cycle. We inherited a florid language from our predecessors to whom catalysis was black magic. Naturally, these words are rather imprecise for a description of catalysis at the molecular level.

Organometallic catalysts consist of a central metal surrounded by organic (and inorganic) ligands. Both the metal and the large variety of ligands determine the properties of the catalyst. The success of organometallic catalysts lies in the relative ease of catalyst modification by changing the ligand environment. Crucial properties to be influenced are the rate of the reaction and the selectivity to certain products.

The following types of selectivity can be distinguished in a chemical reaction:

*chemoselectivity*, when two chemically different functionalities are present such as an alkene and an aldehyde in the example in Figure 1.1 which both can be hydrogenated, the chemoselectivity tells us whether the aldehyde or the alkene is being hydrogenated; or when more than one reaction can take place for the same substrate e.g. hydrogenation or hydroformylation;

*regioselectivity*, as in the example shown for the hydroformylation reaction, the formyl group can be attached to either the primary, terminal carbon atom or the secondary, internal carbon atom, which leads respectively to the linear and the branched product;

*diastereoselectivity*, the substrate contains a stereogenic centre and this together with the catalyst can direct the addition of dihydrogen in the example to give two diastereomers, the selectivity for either one is called the diastereoselectivity;

*enantioselectivity*, the substrate is achiral in this instance, but the enantio-pure or enantio-enriched catalyst may give rise to the formation of one specific product enantiomer.

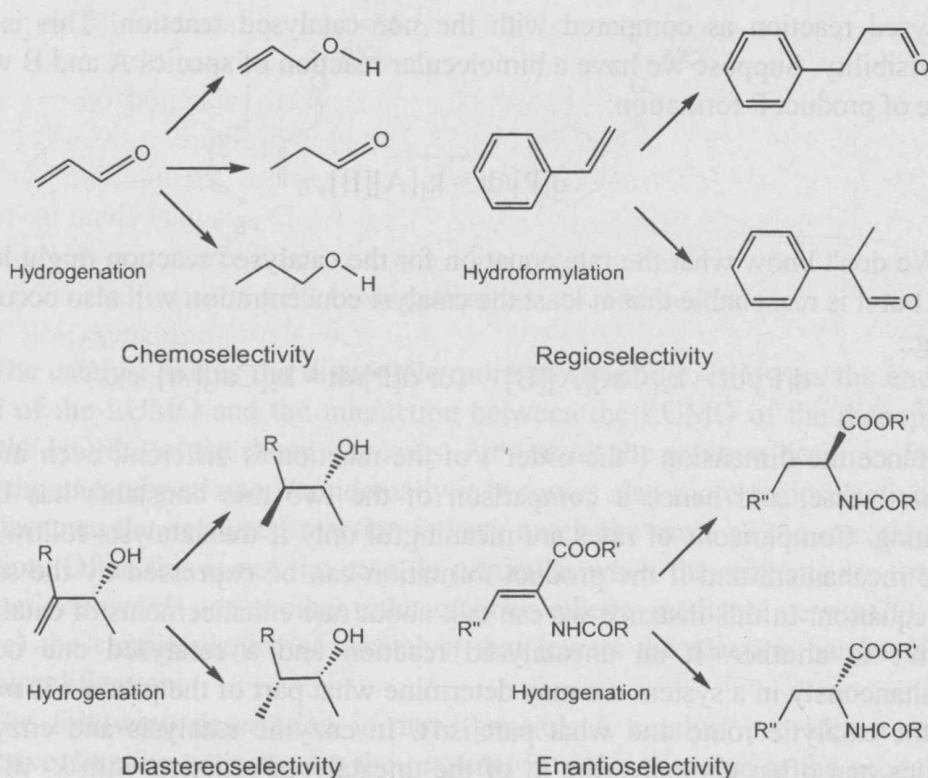


Figure 1.1. Selectivity of chemical conversions

High selectivity is a means

- 1) to reduce waste,
- 2) to reduce the work-up equipment of a plant, and
- 3) to ensure a more effective use of the feedstocks.

Rate enhancements of many orders of magnitude can be obtained in catalysis, often by very subtle changes. Rates represent a cost factor, higher rates allowing higher space-time yields (kg of product per time and reactor volume) and hence smaller reaction vessels. Higher rates and higher overall catalyst yields (i.e. mass of product per unit mass of catalyst) reduce the incremental contribution of catalyst costs per unit mass of product generated: In the case of metallocene catalysts for olefin polymerisation for example (Chapter 10) the higher catalyst cost contribution of these catalysts (around \$0.04 per kg of polyolefin) has significantly reduced their impact and ability to displace Ziegler-Natta catalysts (where the catalyst cost contribution is only \$0.006-0.011 per kg of polymer).

Kinetics are an important part of catalysis; after all, catalysis is concerned with accelerating reactions. In order to describe the effectiveness of a catalyst one would like to determine the acceleration that has been achieved in the



catalysed reaction as compared with the non-catalysed reaction. This is an impossibility. Suppose we have a bimolecular reaction of species A and B with a rate of product P formation:

$$d[P]/dt = k_1[A][B]$$

We don't know what the rate equation for the catalysed reaction might look like, but it is reasonable that at least the catalyst concentration will also occur in it, e.g.:

$$d[P]/dt = k_2[\text{Cat}][A][B] \quad (\text{or } d[P]/dt = k_3[\text{Cat}][A], \text{ etc.})$$

Hence the dimension ("the order") of the reaction is different, even in the simplest case, and hence a comparison of the two rate constants has little meaning. Comparisons of rates are meaningful only if the catalysts follow the same mechanism and if the product formation can be expressed by the same rate equation. In this instance we can talk about rate enhancements of catalysts relative to another. If an uncatalysed reaction and a catalysed one occur simultaneously in a system we may determine what part of the product is made via the catalytic route and what part isn't. In enzyme catalysis and enzyme mimics one often compares the  $k_1$  of the uncatalysed reaction with  $k_2$  of the catalysed reaction; if the mechanisms of the two reactions are the same this may be a useful comparison. A practical yardstick of catalyst performance in industry is the "space-time-yield" mentioned above, that is to say the yield of kg of product per reactor volume per unit of time (e.g. kg product/m<sup>3</sup>.h), assuming that other factors such as catalyst costs, including recycling, and work-up costs remain the same.

In practice the rate equation may take a much more complicated form than the ones shown above. The rate equation may tell us something about the mechanism of the reaction.

Before we turn to "mechanisms" let us repeat how a catalyst works. We can reflux carboxylic acids and alcohols and nothing happens until we add traces of mineral acid that catalyse esterification. We can store ethene in cylinders for ages (until the cylinders have rusted away) without the formation of polyethylene, although the formation of the latter is exothermic by more than 80 kJoule/mol. We can heat methanol and carbon monoxide at 250 °C and 600 bar without acetic acid being formed. After we have added the catalyst the desired products are obtained at a high rate.

A catalyst lowers the barrier of activation of a reaction, i.e. it lowers the activation energy. When protons or Lewis acids are the catalysts this description seems accurate, as for instance in a Diels-Alder reaction (Figure 1.2):



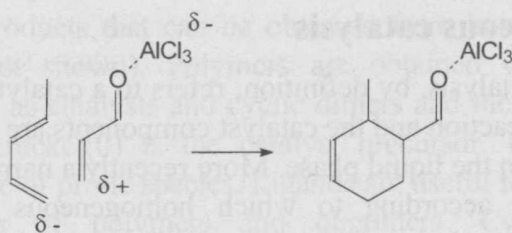


Figure 1.2. Lewis acid catalysis; the "base case"

The catalyst makes the dienophile more electrophilic. It lowers the energy level of the LUMO and the interaction between the LUMO of the dienophile and the HOMO of the diene increases. As a result the reaction becomes faster than the uncatalysed one. Accidentally it becomes also more regioselective. In this instance the catalysed reaction is very much the same as the uncatalysed reaction. Often this is not the case. In particular when the reagents are totally unreactive towards one another (ethene versus ethene, methanol versus CO, see above) the simple picture of a catalyst that lowers the reaction barrier is an oversimplification.

The following description is more general. A catalyst provides a more attractive reaction pathway for the reagents in order to arrive at the products. This new pathway may involve many steps and may be rather complicated. Imagine the direct reaction between methanol and CO. One can calculate what the most likely reaction pathway for the thermal reaction looks like using *ab initio* molecular orbital methods. It may well be that an almost complete dissociation of the methyl and hydroxyl bond is needed before CO starts interacting with the methanol fragments. (The temperature required for this reaction also allows the energetically more attractive formation of methane and CO<sub>2</sub>!) The catalytic reaction involves the formation of methyl iodide, reaction of methyl iodide with a rhodium complex, reaction of the methyl rhodium fragment with co-ordinated CO, etc. which is not quite the simplest and most direct route one can imagine and yet it is the basis of a highly sophisticated catalytic process. The catalyst brings the reagents together in a reactive state. Summarising, *a catalyst provides a new reaction pathway* with a low barrier of activation, which may involve many intermediates and many steps. The sequence of steps we call the mechanism of the reaction. Mechanism also refers to the more detailed description of a reaction at the molecular bonding level. During the process, the catalytic cycle, the catalyst participates in many "complexes" all of which one can call "the" catalyst. It cycles continuously from one species to another. In this sense the catalyst itself remains unchanged during the catalytic conversion (Ostwald, page 1).