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Coordination and Catalysis

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Preface

Catalysis with coordination compounds of transition metals has become, during the past decade, a real forum of encounter for various disciplines of chemistry. Preparative organic chemistry and polymer chemistry are perhaps primarily interested from the point of view of the reaction products, organometallic and inorganic coordination chemistry from the side of the catalytically active transition metal center; the methods of physical chemistry are often extremely helpful in elucidating the mechanism of a catalytic process and, last not least, the conceptions and computational results of theoretical chemistry may guide the catalysis chemist to a better insight into the interactions of catalyst and substrates, at a molecular level.

In particular, catalysis with well defined, soluble transition metal complexes (homogeneous catalysis) plays an eminent role, not only as the medium of very important industrial and laboratory processes such as hydroformylation, hydrogenation, dimerization, oligomerization and polymerization of olefins, etc., but also as a model for heterogeneous processes, the mechanism of which is inherently more difficult to elucidate directly, and even as a model for certain natural enzymatic processes.

The present book deals with such well defined transition metal complexes and their use in catalysis. Some comments concerning the layout of the book may be appropriate. The title "Coordination and Catalysis" indicates a certain division into two parts. The interdisciplinary character of the subject matter has the consequence that the practical chemist, interested in a certain catalytic reaction, very often is not familiar enough with the methods and the special technical jargon used by his colleagues of the contiguous disciplines. Such lack of knowledge may result in a serious handicap during literature studies, and may impede a fruitful cooperation between the various interested groups. The first six chapters of the book are designed to bridge this gap. They provide the basic background of coordination chemistry as far as it is useful or even indispensable for a chemist working with transition metal complexes. In presenting this theoretical background, we kept in mind that it is more important for the practical catalysis chemist to understand the significance of the information available from a specific theory than to be able to apply its often sophisticated mathematics for his own computations.

The chapters "Atomic Orbitals" and "Transition Metal Ions" shall remind the reader of his basic knowledge of atomic structure, with particular emphasis on d orbitals and transition metals. Readers with a background in introductory quantum chemistry will be able to cover these two chapters rather quickly, but we hope that for others they might fill some voids. Informations that should be known from other sources are sometimes treated only very briefly. More space is given to certain details which, from the authors' experience, are often not clearly understood. Thus we have tried to answer such elementary questions as: What is the physical significance of the four-lobe representations of d orbitals, so trustfully used by chemists? Why has one of the d orbitals a different shape? What does the labeling of the d orbitals ($d_{x^2-y^2}$, d_{xz}, etc.) mean? Special care has also been taken to explain the determination of the Russell-Saunders terms of a given d^n configuration.

The following three chapters are dedicated to the three theories which are the basis for all theoretical and semitheoretical work in the field: group theory, ligand field theory and mole-

cular orbital theory. Most modern research publications relative to the matter are written in the language of one or the other of these theories. The concepts of group theory are presented in this book in a rather pragmatic, application oriented fashion. The trained reader may pardon the complete lack of mathematical rigour, but we have endeavoured to treat this valuable device as a tool rather than as a science. In particular the understanding of ligand field theory is greatly facilitated by some basic knowledge of group theory. And ligand field theory, this lucid account of the influences of ligands on the electronic levels of a central transition metal ion in a complex, is indispensable for the comprehension of the electronic spectra and the magnetic properties of such a complex, as well as of its behaviour in catalysis. Group theory is also one of the elements of the molecular orbital theory of transition metal complexes which, in our context, is used to account for all effects and consequences of covalent bonding between the metal center and its ligands.

In the whole of this first part of the book, we have tried to emphasize the relation to practical application, which sometimes gets lost in more sophisticated treatises. We hope that our often deliberately simplifying treatment will stimulate the interested reader to proceed to the more advanced texts which are listed at the end of each chapter (with increasing degree of difficulty, if there are more than one on the same topic).

The application part of the book starts with the chapter "Some Aspects of Catalysis with Transition Metal Complexes", where the present knowledge (and sometimes opinion) concerning the general course of a transition metal catalyzed reaction is discussed in the light of coordination chemistry. This field of work is doubtlessly still in a state of flux, where new hypotheses and suggestions are brought continuously into consideration. Under such conditions it is perhaps inevitable that the chosen presentation occasionally overemphasizes the authors' view.

The following chapters on particular catalytic reactions are organized in such a way as to minimize overlap. Thus, although the accent is generally on mechanistic aspects, and in particular on the processes occurring within the coordination sphere of the transition metal center, the division is according to substrates rather than to metal centers. Reactions of olefins, conjugated diolefins, carbon monoxide, oxygen, and nitrogen are treated, each in a chapter. The first three of these chapters are rigorously restricted to real catalysis, i.e. omitting all stoichiometric reactions of ligands in the coordination sphere of a metal. Sufficient technically important catalytic reactions are available to serve as illustrations for the principles to be discussed. In the last two chapters certain concessions in this respect appeared appropriate. The activation of molecular oxygen and nitrogen are processes produced by nature under mildest conditions, mostly in the presence of a transition metal carrying enzyme. Chemistry is still at the very beginning of learning to understand, and hopefully one day to copy, the work of Nature.

Obviously it was not possible, nor our intent, to include in the application part of the book reference to all papers in the literature concerning the vast field of homogeneous catalysis with transition metal complexes. Very often more recent papers are cited which in most cases refer to the older original papers. This was done generally when the treated material was presented more didactically in the more recent work. The suggested "additional reading" at the end of each of the later chapters refers mostly to review papers which permit the reader to broaden his knowledge on certain catalytic reactions treated in the chapter. Here again, a somewhat subjective selection appears inevitable.

Finally, we would like to indicate for which classes of readers the book has been conceived. Proceeding from the authors' teaching experience at the Swiss Federal Institute of Technology and at the University of Mainz, Germany, the book is addressed, on one hand, to advanced students who wish to specialize in this interesting field. On the other hand, however, we have undertaken a serious effort to make the book suitable for self-study, considering those chemists who completed their studies several years ago and who wish to keep up with modern developments. The expert research chemist working in the field, last not least, will hopefully find sufficient stimulation in the selective compilation of recent research work.

It is a great pleasure to acknowledge the valuable help of our friends and collegues, who read parts of the book and offered many clarifying suggestions: Ph. Teyssié, University of Liège, Belgium; J. Halpern, University of Chicago; L. Markó, University of Veszprem, Hungary; B. Bogdanović, Max-Planck-Institute, Mülheim, Germany; D. A. v. Bézard and E. Spitzer-Wien, Swiss Federal Institute of Technology; Ch. Jungo, University of Fribourg, Switzerland. Furthermore, we greatly appreciate the effort of D.R.M. Walton, University of Sussex, England, in polishing our English.

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Contents

1. Introduction

Catalysis with soluble transition metal complexes has attracted very great interest over the past few decades both because of the novelty of much of the chemistry involved and because of its potential and, as already proven in numerous examples, practical applications. The starting point of this development was probably the discovery by O. Roelen [1] in 1938 of the reaction of olefins with carbon monoxide and hydrogen to form aldehydes (the "oxo process" or hydroformylation), where a soluble cobalt carbonyl complex served as catalyst. Many other homogeneous reactions were subsequently discovered, some of the most important of which are the oxidation of ethylene to acetaldehyde on a palladium complex ("Wacker process") [2], the carbonylation of methanol with a rhodium species [3], the cyclo-oligomerization of conjugated diolefins on nickel [4], and the dimerization [5], oligomerization [6] and polymerization [7] of olefins with soluble Ziegler catalysts.

From a technical point of view, this development was challenged by the availability, at reasonable prices, of olefins after the displacement of coal by natural gas and oil as the most important feedstocks for the chemical industry. In the nineteen forties, coal-based acetylene was still a major raw material in chemical processing (especially in Germany), useful because of its high reactivity. Gradually it has been replaced by ethylene and other olefinic compounds which are less expensive, but where superior catalysts have to compensate for lower reactivity. Another impulse came from a general trend toward milder reaction conditions. The more "classical" processes using heterogeneous metal oxide or metal catalysts are often termed "capital-intensive", meaning that high capital has to be invested per ton of product. This is mainly due to the high pressures and temperatures usually required, with the often disagreeable consequence of reduced selectivity. Moreover, relatively low conversions per pass frequently necessitate the separation of product from highly diluted mixtures, and recycling of the unreacted components.

Homogeneous catalysts, on the other hand, usually work at low pressure and temperature, with high efficiency, and sometimes with an amazing selectivity. Thus, for instance, the manufacture of acetaldehyde from ethylene and oxygen in an aqueous catalyst system by the Wacker process operates at the boiling temperature of water at pressures of only a few atmospheres. This process has displaced the older vapor-phase oxidation of ethyl alcohol in the temperature range 375 to 500 °C. An example of selectivity is the cyclooligomerization of butadiene which can be oriented towards cyclooctadiene or to cyclododecatriene, by only minor variations of the nickel catalyst (20 °C, normal pressure).

Nevertheless, soluble transition metal complexes are by no means expected to replace the heterogeneous metal oxide and metal catalysts in all domains. Their robustness and easy regeneration guarantee them a secure future in catalytic chemistry. However, experiences obtained with soluble catalyst species have also had an impact on heterogeneous catalysis. Most solid catalysts are non-stoichiometric, ill-defined materials; moreover, the fact that the reactions take place at a gas-solid interface implies certain physical complications, such as rate control by mass transfer, influence of pore volume, etc. These conditions are not favorable for a mechanistic interpretation of heterogeneous processes. Work with well-defined soluble complexes has contributed greatly to the understanding of the basic principles of transition metal catalysis which may be assumed to be common to heterogeneous and homogeneous processes. The Fischer-Tropsch reaction, for instance, which comprises

the formation of hydrocarbons from carbon monoxide and hydrogen on heterogeneous cobalt or iron catalysts, and which was very important during the coal-based feedstocks period, is to-day at least partly understood in terms of individual steps recognized in the course of the homogeneous hydroformylation of olefins [8]. The Fischer-Tropsch, and related reactions may revive when the oil reserves decline. The related synthesis of methanol from carbon monoxide and hydrogen is of even more significant interest, as a step in one of the routes from methane (earth gas component) to the easier transportable methanol, which may become an important export capacity from the Middle East in the nineteen eighties [9]. Evidently the discovery of a soluble system for the synthesis of methanol from carbon monoxide and hydrogen would constitute a great step towards its mechanistic elucidation. On the other hand, the ideas gained in the work with soluble complexes have, in certain cases, even stimulated systematic variations of heterogeneous catalysts [10].

Although the discovery of the first soluble catalysts was, presumably, more or less accidental, modern catalysis research appears to be progressing towards an intelligent synthesis of contributions from many sources and from different disciplines of chemistry. In particular, it has benefited greatly from two major scientific developments of the past decades. On one hand, transition metals attracted growing interest in preparative coordination chemistry as a great number of new compounds became available, while on the other hand important advances in theoretical inorganic chemistry (particularly in ligand field theory) influenced the thinking of catalysis chemists. As a result, more and more attention was devoted to the significance of coordination sphere symmetry of a catalytic transition metal center and of the distribution of electron density therein. It was recognized that the metal centers are in a sense polyfunctional, possessing a multisite capability for forming several electron pair bonds in clearly defined geometric juxtaposition, thus predisposing reactants within the framework of a complex towards specific interaction. The influence of certain atoms or groups of atoms attached to a metal center (the "ligands") on the activity of the latter was observed and traced back to the fact that the ligands may either donate electron density to, or withdraw it from the metal.

Two different approaches have led to the present situation of knowledge and concepts. The first, of a phenomenological nature, was aimed at the effectiveness of catalysts and consists essentially of varying parameters and measuring activities. This procedure, with prominent industrial support, has been very successful in several occasions. Thus, the production of aldehydes, acids, esters, etc., by the oxo process and related reactions was able to make "big money" during the many years until a well-argued suggestion concerning the mechanism was advanced in 1961 [11]. The same criterion holds good for low pressure polymerization of ethylene with heterogeneous titanium/aluminum catalysts discovered by Ziegler in 1952 [12], by which millions of tons of polyethylene were procuced world-wide, prior to 1964 when a theoretical interpretation of the process was offered [13], and before the use of analogous soluble catalysts permitted a mechanistic interpretation [7].

The second path of research, located more within the University sphere, is concerned more with the manner in which a catalyzed reaction proceeds. This, the more basic approach, consists of the determination of the sequence of the elementary reactions within the co-ordination sphere of the metal center in the course of a catalytic cycle, measurement of rate and equilibrium constants for these individual steps, isolation or spectroscopic identification of intermediates, and determination of the valency state and coordination number of the active metal center, *etc.*

Much progress has also been achieved by an imaginative transfer of ideas and experience from one catalytic process to another. An illustration is provided by the Ziegler catalysts. The original discovery referred to a combination of an aluminum alkyl and a transition metal salt (in particular triethylaluminum and titanium tetrachloride) as catalyst for the low pressure polymerization of ethylene. While initially the aluminum component was considered as the catalyst, and the transition metal as a "cocatalyst", careful fundamental work in several laboratories, with related soluble systems, led to the conclusion that the transition metal is the active center, and that the aluminum alkyl can carry out one or more of several tasks: It can alkylate the transition metal center, forming an active metal-carbon bond. If the metal alkyl is unstable, and is homolytically cleaved, the aluminum alkyl provokes indirectly reduction of the transition metal ion, thus bringing the latter eventually into a valency state required for catalysis. Finally, the aluminum alkyl can form a complex with the transition metal center, operating as an activating ligand. This multipurpose action of aluminum alkyls in Ziegler systems once recognized, it was a logical corollary to use these systems not only for polymerization, but also in other cases where the *in situ* formation of low valent and/or alkylated transition metal species was required for catalysis. In this way, Ziegler systems have found ample application in many catalytic reactions, such as the dimerization of olefins and of conjugated diolefins, metathesis, and even hydrogenation of olefins.

From these few introductory remarks it will be evident that our treatment of the phenomenon catalysis by coordination compounds of transition metals will emphasise those processes occurring within the coordination sphere of the metal center more than the technical aspects of the catalytic reactions. In this sense, we considered it useful to initiate the book with a basic consideration of the electronic structure of transition metal ions, and with the theoretical concepts underlying their coordination chemistry which have contributed greatly to the understanding of transition metal catalysis. The most essential concepts stem from group theory, ligand field theory and molecular orbital theory. With regard to the latter two it should, however, always be born in mind that they represent approximations, and that our exact knowledge of bonding in coordination compounds (and of chemical bonding in general) is far from being complete. Nevertheless, these theories have provided us with extremely useful interpretations of certain aspects of the bonding in transition metal complexes, and of properties of the complexes depending thereupon (*e.g.* spin pairing of electrons in d orbitals and magnetism; directed valency and symmetry; electron distribution and activity; *etc.*).

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2. Atomic Orbitals

In this section we shall summarize briefly the quantum mechanical treatment of the hydrogen atom. This will remind the reader of the origin of our working knowledge about the geometry and directional properties of atomic orbitals.

2.1. Wave Equation and Wave Functions

In 1926 the chemist's electron was displaced by the quantum mechanicist's electron. The chemist's electron was a small particle, moving in a defined circular or elliptic orbit around the nucleus of an atom (Bohr-Sommerfeld model). Quantum mechanics tells us that the electron is comparable to a standing wave which can be described by a wave equation. The starting point for this development was de Broglie's wave theory of matter (1924), which was based on theoretical as well as metaphysical considerations. At that time, it had become evident that light, apparently well-defined as a wave process since Fresnel, can also be described as a corpuscle. The belief in a general harmony in Nature led de Broglie to the ingenious assumption that a wave-particle dualism would also apply to matter. He formulated the relationship between wave length λ, mass m, and velocity v of a particle:

$$\lambda = \frac{h}{m \cdot v} \tag{2.1}$$

where h is Planck's constant. The formulation of a wave equation for the electron by Schrödinger (1926) was a logical corollary of these ideas. Experimentally, the wave-particle dualism manifests itself through the observation of both diffraction patterns and interferences, with particles (electrons, protons, *etc.*) as well as with electromagnetic radiation (light, X-rays).

Fortunately some of the properties of the electron, interesting for the chemist, are such that they still may be rationalized by the classical concept, and in view of the wave-particle dualism we are allowed to do so whenever it appears convenient. Other properties, however,
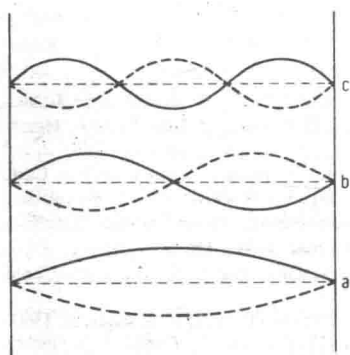

Fig. 2.1. The classical standing wave; fundamental wave (a), and first (b) and second (c) overtones.