

ACTIVATION AND CATALYTIC REACTIONS OF SATURATED  
HYDROCARBONS IN THE PRESENCE OF METAL COMPLEXES

# Catalysis by Metal Complexes

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Volume 21

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# ACTIVATION AND CATALYTIC REACTIONS OF SATURATED HYDROCARBONS IN THE PRESENCE OF METAL COMPLEXES

by

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## PREFACE

Chemistry is the science about breaking and forming of bonds between atoms. One of the most important processes for organic chemistry is breaking bonds C–H, as well as C–C in various compounds, and primarily, in hydrocarbons. Among hydrocarbons, saturated hydrocarbons, alkanes (methane, ethane, propane, hexane etc.), are especially attractive as substrates for chemical transformations. This is because, on the one hand, alkanes are the main constituents of oil and natural gas, and consequently are the principal feedstocks for chemical industry. On the other hand, these substances are known to be the less reactive organic compounds. Saturated hydrocarbons may be called the “noble gases of organic chemistry” and, if so, the first representative of their family – methane – may be compared with extremely inert helium. As in all comparisons, this parallel between noble gases and alkanes is not fully accurate. Indeed the transformations of alkanes, including methane, have been known for a long time. These reactions involve the interaction with molecular oxygen from air (burning – the main source of energy!), as well as some mutual interconversions of saturated and unsaturated hydrocarbons. However, all these transformations occur at elevated temperatures (higher than 300–500 °C) and are usually characterized by a lack of selectivity. The conversion of alkanes into carbon dioxide and water during burning is an extremely valuable process – but not from a chemist viewpoint.

The chemical inertness of alkanes can be overcome if the transformations are carried out at high temperatures. However, the low selectivity of such processes motivates chemists into searching principally for new routes of alkane conversion which could transform them into very valuable products (hydroperoxides, alcohols, aldehydes, ketones, carboxylic acids, olefins, aromatic compounds etc.) under mild conditions and selectively. This is also connected with the necessity for the development of intensive technologies and for solving

the problems of ecology. Finally, one more very important problem is the complete and efficient chemical processing of oil and gas components, which becomes pertinent because of gradual depletion of hydrocarbon natural resources.

In the last decades, new reactions of saturated hydrocarbons under mild conditions have been discovered. For example, new reactions include alkane transformations in superacid media, interactions with metal atoms and ions, and reactions with some radicals and carbenes. In the same period, the development of coordination metal-complex catalysis led to the discovery of the ability of various types of molecules, including molecular hydrogen, carbon monoxide, oxygen, nitrogen, olefins, acetylenes, aromatic compounds, to take part in catalytic reactions in homogeneous solutions. In such processes, a molecule or its fragment entering the coordination sphere of the metal complex, as a ligand, is chemically activated. It means that a molecule or its fragment attains the ability to enter into reactions that either do not proceed in the absence of a metal complex or occur at very slow rates. At last, the list of compounds capable of being activated by metal complexes has been enriched with alkanes.

This monograph is devoted to the activation and various transformations of saturated hydrocarbons, i.e., reactions accompanied by the C–H and C–C bond cleavage. A special attention is paid to the recently found reactions with the alkane activation in the presence of metal complexes being described in more detail. In addition to the reactions of saturated hydrocarbons which are the main topic of this book, the activation of C–H bonds in arenes and even olefins and acetylenes is considered. In some cases, this activation exhibits similarities for all types of compounds, and sometimes they proceed by different mechanistic pathways.

Chapter I discusses some general questions relevant to the chemistry of alkanes and especially their reactions with metal compounds. Transformations of saturated hydrocarbons in the absence of metal derivatives and in the presence of solid metal and metal oxide surfaces are described in Chapters II and III (Figure 1). Since these reactions are not the main topic of the monograph their consideration here is far from comprehensiveness but the knowledge of such processes is very important for understanding the peculiarities and mechanisms of the reactions with metal complexes. Chapters IV–X are the main chapters of this book because they describe the activation of hydrocarbons in the presence of

metal complexes. Finally, Chapter XI is devoted to a brief description of the hydrocarbon reactions with enzymes, which mainly contain metal ions and are true metal complexes.

We clearly understand that this monograph does not cover all references that have appeared on the reactions of alkanes and other hydrocarbons with metal

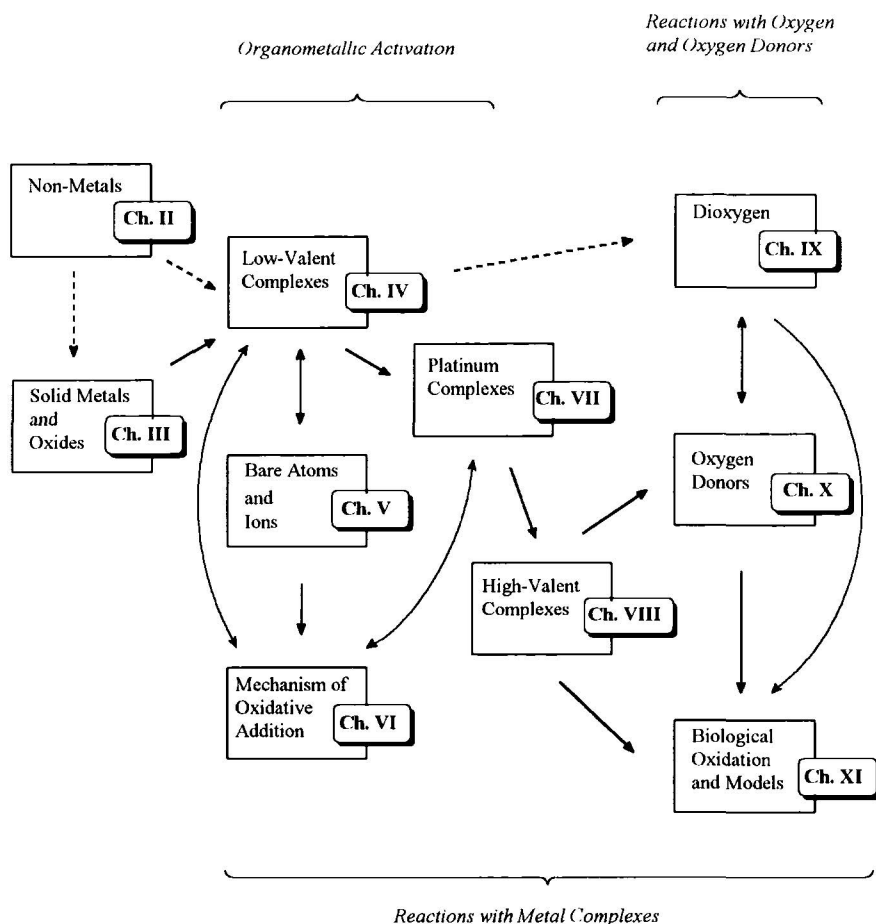


Figure 1. Structure of this monograph.

\* ————— \*

complexes (and especially with various reagents that are not metal complexes). Moreover, we suspect that not all interesting works on alkane activation will be described here in proper detail and some important findings will not be referenced in this edition. We wish to apologize in advance to all scientists who decide that their works are covered too briefly. The subjective factor here is very great. In searching and selecting the references for various chapters, we gave the preferences to recent publications assuming that the reader will be able to find many publications on a certain topic having only one very recent paper. In some cases, we restricted our citation by a review and a few recent original publications (this is especially necessary for citation of works on heterogeneous activation on solid catalysts where the total number of papers is enormous). We tried also to give more detailed descriptions of some hard to obtain works (e.g., published in Russian.). The material of our previous reviews and books published either in Russian or English have been partially used in this monograph.

The authors hope that this book will be useful not only for those who are interested in activation of alkanes and other hydrocarbons by metal complexes, but also for the specialists in homogeneous and heterogeneous catalysis, petrochemistry, and organometallic chemistry. Some parts of the monograph will be interesting for the specialists in inorganic and organic chemistry, theoretical chemistry, biochemistry and even biology, and also for those who work in petrochemical industry and industrial organic synthesis. This book covers studies which appeared up to early 1999.

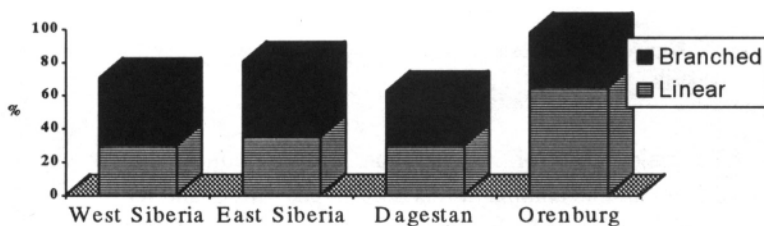
We are grateful to the scientists who have helped to create this book, who discussed with us certain problems of alkane activation, and also provided us with reprints and manuscripts: D. M. Camaioni, B. Chaudret, E. G. Derouane, R. H. Fish, Y. Fujiwara, A. S. Goldman, T. Higuchi, C. L. Hill, Y. Ishii, B. R. James, G. V. Nizova, A. Kitaygorodskiy, the late R. S. Drago, D. R. Ketchum, J. A. Labinger, J. R. Lindsay Smith, J. M. Mayer, J. Muzart, L. Nice, R. A. Periana, E. S. Rudakov, S. Sakaguchi, U. Schuchardt, H. Schwarz, A. Sen, A. A. Shteinman, G. Süss-Fink and many others.

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## INTRODUCTION

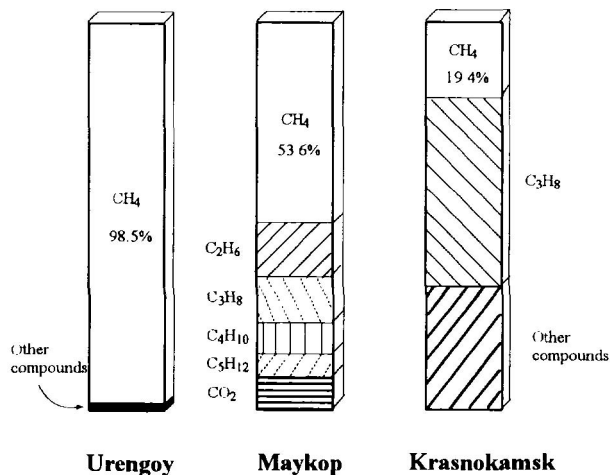
Hydrocarbons occurring in oil and natural gas are of great significance for the contemporary civilization, due to their being the most commonly used fuel, on the one hand, and the source of raw materials for chemical industry, on the other hand [1]. Oil contains (see examples in Figure 2) a considerable amount of alkanes, as well as, aromatic and other hydrocarbons. Methane is usually a major component of natural gas (Figure 3) [2]. The distribution of total natural gas reserves (4,933 trillion cubic feet or  $1.4 \times 10^{11} \text{ m}^3$ ) is the following: Eastern Europe (40.1%), Africa/Middle East (39.2%), Asia-Pacific (6.6%), North America (6.1%), Latin America (4.1%), and Western Europe (3.9%) [1c].



**Figure 2.** Alkane content (%) in petroleum fraction 28-200 °C from certain Russian oil deposits.

Oil cracking gives additional amounts of lower alkanes and olefins, the latter being even more valuable products. Methane and other alkanes are also contained in gases evolved in coal mines; saturated hydrocarbons are obtained by hydrogenation and dry distillation of coal and peat [3a-c]. Paraffins may be produced synthetically, i.e., an alkane mixture is formed of carbon monoxide and

hydrogen (Fischer-Tropsch synthesis); multiring aromatics can be converted to isoparaffins and cycloparaffins [3d]. Polymeric materials including natural products are also the source of alkanes [4]. Finally, alkanes are involved during some biochemical processes [5].



**Figure 3.** Composition of natural gas (volume %) from different Russian deposits.

The major field of hydrocarbon consumption is power supply. Energy evolved from alkane combustion is used in gas, diesel and jet engines. Nowadays, chemical processing of hydrocarbon raw materials, in particular alkanes, requires usually participation of heterogeneous catalysts and elevated temperatures (above 200–300 °C) [6]. Natural gas is used mainly in the production of synthesis gas or hydrogen [6e]. Liquefiable components of natural gas find more extensive application. In the USA, the gas condensate and other liquefied components account for 18% of the overall production of liquid hydrocarbons and 70% of the raw material for the production of ethene and other valuable products.

It should be noted that some processes that proceed at relatively low temperatures are well known – chain radical and microbiological oxidation. Biological transformations of alkanes and other hydrocarbons are extremely



\* \_\_\_\_\_ \*

important because they give convenient routes to valuable chemical products [7]. For example, the bacterial enzyme methane monooxygenase converts about  $10^9$  tons per year of methane to methanol. Besides, they are the basis for the microbiological remediation of soil and waters of seas, rivers and lakes polluted with oil and products of petrochemical industry [8].

The interest in new reactions of alkanes is prompted mainly by the need for selective and efficient industrial transformations of hydrocarbons from oil, gas and coal. Development of this area is necessary because fundamentally new routes from hydrocarbons to valuable products, for example, alcohols, ketones, acids and peroxides, may be discovered. In addition, important environmental problems might be solved using such types of transformations, for instance, the removal of petroleum pollution. However, well-known chemical inertness of alkanes causes great difficulties in their activation especially under mild conditions. Thus, efficient reactions of saturated hydrocarbons with various reagents and particularly with metal complexes make it an extremely difficult, but also excitedly interesting and important problem both for industry and academic theoretical science. Only in the past decades, the vigorous development of metal-complex catalysis allowed the beginning of an essentially new chemistry of alkanes and enriched the knowledge about transformations of unsaturated hydrocarbons. Transformations of hydrocarbons (both saturated and unsaturated) under the action of metal complexes, particularly when these complexes play a role of catalysts, seems to be a very promising field. Indeed, in contrast to almost all presently employed processes, reactions with metal complexes occur at low temperatures and can be selective.

Several monographs [9] and many reviews [10], wholly or partly devoted to the metal complex activation of C–H and C–C bonds in hydrocarbons, appeared in recent decades. Reviews and books devoted to some more narrow topics will be cited later throughout this book.

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