Homogeneous Catalysis
with Metal Complexes
Homogeneous Catalysis
with Metal Complexes

Kinetic Aspects and Mechanisms

O. N. TEMKIN
M.V. Lomonosov Moscow State University of Fine Chemical Technology

Translated from the Russian
by P. P. Pozdeev
To My Wife and Friend,
Raisa Vasil’evna Basova,
with Gratitude for Everything
## Contents

*Notations and Abbreviations*  
*Preface to English Edition*  
*Preface*  
*Acknowledgments*  
*About the Author*

### Introduction

1. **State-of-the-Art in the Theory of Kinetics of Complex Reactions**
   1.1 Main concepts of the Horiuti–Temkin theory of steady-state reactions  
      1.1.1 Reaction mechanism: Stoichiometry and routes  
      1.1.2 Kinetics: Reaction rates with respect to substances and over routes  
      1.1.3 Kinetic polynomial  
      1.1.4 Determining the number of independent parameters in a kinetic model. The problem of identifiability of parameters  
   1.2 Quasi-steady-state and quasi-equilibrium approximations in chemical kinetics  
      1.2.1 Theoretical criteria of quasi-steady-state intermediate concentrations and quasi-equilibrium steps  
      1.2.2 Experimental criteria of applicability of quasi-steady-state approximation in various systems  
   1.3 Methods of graph theory in chemical kinetics and in theory of complex reaction mechanisms  
      1.3.1 Linear mechanisms  
      1.3.2 Nonlinear mechanisms  
      1.3.3 Other fields of application of kinetic and bipartite graphs in chemical kinetics and in theory of complex reaction mechanisms  
   1.4 Elementary steps – Selection rules  
      1.4.1 Main postulates, laws, and principles  
      1.4.2 Energy selection rules for elementary steps  
      1.4.3 Quantum-chemical selection rules for elementary steps  
      1.4.4 Topological selection rules for elementary steps  

### Complexity Functions of Catalysts and Reactants in Reactions Involving Metal Complexes

2.1 Mononuclear metal complexes  
   2.1.1 Complexity functions: variants I and II  
   2.1.2 Complexity functions: variants III and IV  
   2.1.3 General problems and recommendations
2.2 Polynuclear complexes in homogeneous catalytic and noncatalytic reactions
- Systems with formation of associates
- Systems with mononuclear and polynuclear complexes of various types

2.3 Catalysis with polynuclear copper(I) halide complexes in superconcentrated solutions
- Copper(I) chloride complexes in solution and in crystalline state
- Kinetics of catalytic reactions of alkynes in concentrated $\text{NH}_4\text{Cl}–\text{CuCl}_2$ aqueous solutions at constant complexity functions $F_{\text{Cu}}$ and $F_{\text{Cl}}$
- Determination of compositions of catalytically active copper(I) complexes in various reactions
- Studying $\pi$ and $\sigma$ complexes of copper(I) with alkynes in crystalline state and in solution
- Mechanisms of acetylene dimerization and hydrocyanation reactions. Crystallochemical aspects

References

3 Multi-Route Mechanisms in Reactions Involving Metal Complexes
- Factors accounting for the appearance and kinetic features of multi-route mechanisms
- Analysis of multi-route reaction kinetics
- Conjugation nodes and artificial multi-route character
- Conjugate processes
  - Classical approach
  - Kinetic and thermodynamic conjugation in consecutive reactions
  - Conjugation in chain reactions
  - Conclusions

References

4 Polyfunctional Catalytic Systems
- Oxidation reactions of organic and inorganic compounds
  - Oxidation of alkenes
  - Oxidation of 1,3-dienes
  - Oxidation of alkynes and arenes
  - Oxidation of inorganic compounds
- Reactions of chlorination and oxidative chlorination of organic compounds
  - Oxidative chlorination of alkynes
  - Oxidative chlorination of 1,3-dienes
- Polyfunctional catalytic systems in chlorination reactions
- Oxidative carbynylation of organic compounds
  - Oxidative carbynylation of HY molecules ($Y = \text{OR, OPh, NR}_2, \text{Ar, Alk}$)
  - Oxidative carbynylation of alkenes, dienes, and alkynes
- Additive carbynylation of alkynes, alkenes, dienes, and alcohols
- Substitution and addition reactions in alkyne chemistry
- General problems in PFCS theory and practice
  - PFCSs and principles of their functioning
  - Kinetic and chemical functions of $p$-benzoquinone and other quinones in PFCSs
  - Variants of association of catalytic reactions and catalytic systems

References
5 Mechanisms of Formation of Catalytically Active Metal Complexes 453

5.1 Main stages of catalytic process 454

5.2 Chemical reactions involved in the formation of active centers 457

5.3 Mechanisms of active center formation in particular processes 468

5.3.1 Mechanisms of active metal complex formation in PdBr$_2$–LiBr–P(OPh)$_3$–HBr–$n$-C$_4$H$_9$OH catalytic system for acrylate synthesis 468

5.3.2 Carbene metal complexes in metathesis of olefins and analogous processes 471

5.3.3 Mechanisms of 1-butene isomerization in Ni[P(OEt)$_3$]$_4$–H$_2$SO$_4$–MeOH system 488

5.3.4 Features of the formation and decay of active centers in acrylic derivatives synthesis by the Reppe Method 490

5.3.5 Protecting active centers by catalytic process from destruction 492

5.3.6 Mechanism of active center formation in Pd(OAc)$_2$–PPh$_3$–p-benzoquinone–MeOH catalytic system for alkyne oxidative carbonylation at ≡C–H bond 494

5.3.7 Catalysis with small palladium(I) halide and carbonyl halide clusters 499

5.3.8 Mechanisms of formation of large cluster complexes and microheterogeneous nanoparticles 507

5.3.9 Synthesis and characterization of giant palladium clusters 512

5.3.10 Approaches to identification of the nature of catalytically active species in solutions of metal complexes 513

5.4 Examples of chain mechanisms and chain carriers of various natures 518

5.5 Classification of mechanisms of real catalytic processes 528

References 536

6 Nonlinear Effects (Critical Phenomena) in Reaction Dynamics in Homogeneous Catalysis with Metal Complexes 545

6.1 Historical notes 548

6.2 Physicochemical factors responsible for the critical phenomena in homogeneous reactions 551

6.2.1 Thermodynamic features of nonequilibrium processes near and far from equilibrium 552

6.2.2 Dynamic behavior of systems with linear mechanisms in open reactors with complete mixing 565

6.2.3 Nonlinearity of kinetic models 570

6.2.4 Main principles and methods of analysis of the dynamic behavior of nonlinear systems 573

6.3 Analysis of simple nonlinear kinetic models 582

6.4 Mechanisms of oscillatory catalytic reactions 630

6.4.1 Belousov–Zhabotinskii reaction (BZ reaction) 630

6.4.2 Liquid-phase oxidation of organic compounds by oxygen in Co(OAc)$_2$–Br–CH$_3$COOH system 640

6.4.3 Oxidative carbonylation of alkynes in solutions of palladium complexes 644

References 658

7 Rational Strategy for Designing Kinetic Models and Studying Complex Reaction Mechanisms 665

7.1 Stages in the development of chemical kinetics and methodological aspects of the strategy of studying complex reaction mechanisms 666
7.2 Alternative strategies for studying complex reaction mechanisms and designing kinetic models 669
7.2.1 Traditional strategy 669
7.2.2 Rational strategy 671
7.3 Hypothesis generation methods and examples 674
7.4 Hypothesis generation programs: Application examples and related problems 677
7.4.1 Combinatorics on kinetic graphs 677
7.4.2 ChemComb (Comb 1) program 686
7.4.3 MECHEM program 691
7.4.4 NetGen program 694
7.4.5 TAMREAC program 697
7.4.6 ChemNet program 697
7.4.7 Large reaction networks and problems in discrimination of hypotheses and construction of compact kinetic models 713
References 733

8 Effect of Medium on Reaction Rates in Homogeneous Catalysis with Metal Complexes 741
8.1 Effect of electrolytes on the activity coefficients of reaction medium components 743
8.2 Effect of electrolytes on the solubility of nonelectrolytes (gases and organic compounds) 748
8.3 Effect of electrolytes on the rates of elementary reactions between ions and uncharged substrates 752
8.4 Kinetics of catalytic reactions in concentrated aqueous electrolyte (HCl) solutions 754
8.5 Organic solvents in homogeneous catalysis with metal complexes 760
8.5.1 Main physical and chemical properties of solvents 760
8.5.2 Association of solvents and formation of molecular complexes 763
8.5.3 Metal complexes in organic and aqueous-organic solvents 765
8.5.4 Ion association, ion pairs, and specific salt effect in organic solvents 771
8.6 Strong protonic acids in organic solvents and kinetics of catalytic reactions with metal complexes in these media 775
8.6.1 Structure and properties of strong acid solutions in organic solvents 776
8.6.2 Kinetics of catalytic reactions in HCl–NMP, HCl–C₂H₅OH, and HCl–C₂H₅OH–CH₃CN systems 783
8.7 Ionic liquids in catalytic chemistry 787
References 791

Conclusion 797
Subject Index 801
Index of Metals 803
Index of Reactions 805
Notations and Abbreviations

Notations:

\(A\) reaction affinity
\(a\) activity of molecules or ions
\(an\) acceptor number of a solvent molecule
\(B_m\) stoichiometric matrix of reaction mechanism
\(B_N\) stoichiometric submatrix of reaction participants
\(B_p\) stoichiometric matrix of overall route equations
\(B_X\) stoichiometric submatrix of intermediates
\(C^{±}\) cyclic characteristic of a kinetic graph
\(C_A\) concentration of substance A
\(C_{pn}\) weight of \(n\)th cycle on \(p\)th route
\(C_X\) concentration of substance X
\(D_i\) weight of the graph root determinant in \(i\)th vertex
\(D_{ik}\) weight of \(k\)th rooted tree in \(i\)th vertex
\(dn\) donor number of a solvent molecule
\(D_{pn}\) weight of subgraph of \(n\)th cycle on \(p\)th route
\(E^{\varnothing}\) standard electrode potential
\(ee\) enantiomer excess
\(F_i^*\) complexity of \(i\)th intermediate (\(i\)th vertex)
\(F_M\) complexity of metal catalyst
\(F_S\) complexity of substrate
\(G\) matrix of stoichiometric numbers of steps
\(G\) Gibbs energy
\(H\) atomic (molecular) matrix
\(H_0\) Hammet acidity function
\(h_0\) Hammet acidity
\(I\) number of intermediates; ionic strength; induction factor; indicator ratio
\(K\) reaction equilibrium constant
\(k_j\) reaction rate constant
\(n\) average coordination number; Bjerrum formation function
\(N\) number of reaction participants (reactants and products)
\(N_i\) number of linearly independent intermediates
\(P\) number of linearly independent routes (basis set of routes); pressure
\(Q_{max}\) maximum number of linearly independent reactions (in stoichiometric basis set)
\(Q_r\) number of linearly independent overall route equations
\(r\) reaction rate
\( r^{(p)} \) reaction rate over \( p \)th route
\( r^\pm \) reaction rates in forward (+) and reverse (−) direction

\( S \) number of steps in reaction mechanism

\( W_j \) rate on \( j \)th steps

\([X]\) concentration of substance \( X \)

\( \alpha \) gas distribution coefficient between gaseous phase and solution

\( \alpha_i \) polarizability of \( i \)th substance (or solvent)

\( \beta_{ij}^n \) stoichiometric coefficient of \( i \)th intermediate at \( j \)th step

\( \beta_{12} \) exchange integral

\( \chi \) degree of conversion

\( \varepsilon \) small parameter; concentration fluctuation; dielectric permittivity

\( \varepsilon_i \) extinction coefficient

\( \gamma \) kinetic chain length; activity coefficient

\( \gamma_i \) activity coefficient (molar)

\( \eta \) viscosity small parameter

\( \mu \) chemical potential; molecularity of step; dipole moment

\( \sigma \) surface tension

\( \nu_j^{(p)} \) stoichiometric number of \( j \)th step in \( p \)th route

\( \xi \) extent of reaction; chemical variable

\( \omega_j \) weight of \( j \)th step

**Abbreviations:**

- AA acrylic acid
- AC acetone
- Ac acetyl
- acac acetylacetonate (anion)
- acacH acetylacetone
- AcO acetate anion
- AcOH acetic acid
- ADMA acetaldehyde dimethyl acetal (1,1-dimethoxyethane)
- ADN adipodinitrile
- ADP adenosine diphosphate
- Alk alkyl
- All allyl
- AN acetonitrile
- AP acetophenone (methyl phenyl ketone)
- ATP adenosine triphosphate
- BA butyl acrylate
- BDM dibutyl dihydromuconate
- BEE 2-bromoethyl ethyl ether (1-bromo-2-ethoxyethane)
- BG bipartite graph (nonlinear mechanism)
- BG\( _X \) subnetwork of intermediates \( X \) in bipartite graph
- bipy 2,2'-bipiridyl
- BME 2-bromoethyl methyl ether (1-bromo-2-methoxyethane)
<table>
<thead>
<tr>
<th>Notation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>[bmim]⁺</td>
<td>1-bityl-3-methylimidazolium cation</td>
</tr>
<tr>
<td>BP</td>
<td>benzoyl peroxide</td>
</tr>
<tr>
<td>BQ</td>
<td>para-benzoquinone</td>
</tr>
<tr>
<td>Bu</td>
<td>butyl</td>
</tr>
<tr>
<td>Bu⁺</td>
<td>tert-butyl</td>
</tr>
<tr>
<td>Bz</td>
<td>benzoyl</td>
</tr>
<tr>
<td>CB</td>
<td>chlorobutadiene</td>
</tr>
<tr>
<td>CH</td>
<td>cyclohexene</td>
</tr>
<tr>
<td>CHA</td>
<td>cyclohexanecarboxylic acid</td>
</tr>
<tr>
<td>CME</td>
<td>2-chloroethyl methyl ether (1-chloro-2-methoxyethane)</td>
</tr>
<tr>
<td>CSTR</td>
<td>continuous-flow stirred tank reactor</td>
</tr>
<tr>
<td>Cod</td>
<td>1,5-cyclooctadiene</td>
</tr>
<tr>
<td>Cot</td>
<td>cyclooctatetraene</td>
</tr>
<tr>
<td>Cp</td>
<td>cyclooctapentadienyl</td>
</tr>
<tr>
<td>CQ</td>
<td>chloranil (tetrachloro-p-benzoquinone)</td>
</tr>
<tr>
<td>CVA</td>
<td>2-chlorovinylacetylene (2-chloro-1-but-3-ine)</td>
</tr>
<tr>
<td>Cy</td>
<td>cyclooctene, cyclohexyl</td>
</tr>
<tr>
<td>DA</td>
<td>diacetylene</td>
</tr>
<tr>
<td>dba</td>
<td>dibenzilydeneacetone</td>
</tr>
<tr>
<td>DCA</td>
<td>dichloroacetylene</td>
</tr>
<tr>
<td>DCE</td>
<td>1,2-dichloroethylene</td>
</tr>
<tr>
<td>DIOP</td>
<td>2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolan</td>
</tr>
<tr>
<td>DMC</td>
<td>dimethyl carbonate</td>
</tr>
<tr>
<td>DMDA</td>
<td>dimethylidiacetylene</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DMO</td>
<td>dimethyl oxalate</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>dppe</td>
<td>1,2-bis(diphenylphosphin)ethane (diphenylphosphinoethane)</td>
</tr>
<tr>
<td>dppe</td>
<td>1,2-bis(diphenylphosphin)methane (diphenylphosphinomethane)</td>
</tr>
<tr>
<td>DQ</td>
<td>duroquinone (tetramethyl-p-benzoquinone)</td>
</tr>
<tr>
<td>dtc</td>
<td>diethyli thiocarbamate</td>
</tr>
<tr>
<td>DVA</td>
<td>1,2-divinylacetylene</td>
</tr>
<tr>
<td>EA</td>
<td>ethyl acetate</td>
</tr>
<tr>
<td>[emim]⁺</td>
<td>1-ethyl -3-methylimidazolium cation</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>GA</td>
<td>glycolate anion</td>
</tr>
<tr>
<td>GBL</td>
<td>γ-butyrolactone</td>
</tr>
<tr>
<td>Hal</td>
<td>halogenide (halide)</td>
</tr>
<tr>
<td>HE</td>
<td>halide ethers</td>
</tr>
<tr>
<td>HFB</td>
<td>hexafluorobenzene</td>
</tr>
<tr>
<td>HMPTA</td>
<td>hexamethylphosphoric triamide</td>
</tr>
<tr>
<td>HP</td>
<td>hydroperoxide</td>
</tr>
<tr>
<td>HPA</td>
<td>heteropolyacid</td>
</tr>
<tr>
<td>IL</td>
<td>ionic liquid</td>
</tr>
<tr>
<td>Im</td>
<td>imidazole</td>
</tr>
<tr>
<td>Notation</td>
<td>Description</td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
</tr>
<tr>
<td>IP</td>
<td>ion pair</td>
</tr>
<tr>
<td>KF</td>
<td>kinetic function</td>
</tr>
<tr>
<td>KG</td>
<td>kinetic graph (subnetwork of intermediates in linear mechanism)</td>
</tr>
<tr>
<td>KIE</td>
<td>kinetic isotope effect</td>
</tr>
<tr>
<td>LTI</td>
<td>labeled topology identifier</td>
</tr>
<tr>
<td>MCA</td>
<td>monochloroacetylene</td>
</tr>
<tr>
<td>MCS</td>
<td>multicomponent system</td>
</tr>
<tr>
<td>MDA</td>
<td>methylidiacetylene</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>Mes</td>
<td>2,4,6-trimethylphenyl</td>
</tr>
<tr>
<td>MMA</td>
<td>methylmethacrylate</td>
</tr>
<tr>
<td>MO</td>
<td>molecular orbital</td>
</tr>
<tr>
<td>MP</td>
<td>methyl propionate</td>
</tr>
<tr>
<td>MSA</td>
<td>methanesulfonic acid</td>
</tr>
<tr>
<td>MSS</td>
<td>multiplicity of steady states</td>
</tr>
<tr>
<td>NADH</td>
<td>nicotinamide adenine dinucleotide</td>
</tr>
<tr>
<td>NBD</td>
<td>norbornadiene</td>
</tr>
<tr>
<td>NC</td>
<td>nanocluster</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methylpyrroolidone</td>
</tr>
<tr>
<td>NQ</td>
<td>\textit{para}-naphthoquinone</td>
</tr>
<tr>
<td>Nu</td>
<td>nucleophile</td>
</tr>
<tr>
<td>Oc</td>
<td>octene</td>
</tr>
<tr>
<td>OEP</td>
<td>octaethylporphyrinato anion</td>
</tr>
<tr>
<td>Ol</td>
<td>olefine</td>
</tr>
<tr>
<td>Ox</td>
<td>oxidant</td>
</tr>
<tr>
<td>PA</td>
<td>phenylacetylene</td>
</tr>
<tr>
<td>Pc</td>
<td>phthalocyaninato anion</td>
</tr>
<tr>
<td>\textit{p-cymol}</td>
<td>\textit{para}-cymol (\textit{para}-methylisopropylbenzene)</td>
</tr>
<tr>
<td>PE</td>
<td>quasi-equilibrium (pre-equilibrium) approximation</td>
</tr>
<tr>
<td>PEG</td>
<td>polyethylene glycol</td>
</tr>
<tr>
<td>PFCS</td>
<td>polyfunctional catalytic system</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>Phen</td>
<td>1,10-phenanthroline</td>
</tr>
<tr>
<td>Pipy</td>
<td>piperidine</td>
</tr>
<tr>
<td>Pr</td>
<td>propyl</td>
</tr>
<tr>
<td>Py</td>
<td>pyridine</td>
</tr>
<tr>
<td>Q</td>
<td>quinone</td>
</tr>
<tr>
<td>Red</td>
<td>reductant</td>
</tr>
<tr>
<td>RN</td>
<td>reaction network</td>
</tr>
<tr>
<td>SA</td>
<td>succinic anhydride</td>
</tr>
<tr>
<td>salen</td>
<td>N, N'-ethylene-bis(salicylideminato) anion</td>
</tr>
<tr>
<td>Salophen</td>
<td>N, N'-phenylene-bis(salicylideminato) anion</td>
</tr>
<tr>
<td>SS</td>
<td>quasi-steady-state approximation</td>
</tr>
<tr>
<td>SSM</td>
<td>simple submechanism</td>
</tr>
<tr>
<td>TCE</td>
<td>trichloroethylene; tetrachloroethane</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TI</td>
<td>transition-state-topology identificator</td>
</tr>
<tr>
<td>tmeda</td>
<td>1,2-bis(dimethylamino)ethane (tetramethylethylenediamine)</td>
</tr>
<tr>
<td>TOF</td>
<td>catalyst turnover frequency</td>
</tr>
<tr>
<td>TON</td>
<td>catalyst turnover number</td>
</tr>
<tr>
<td>TPP</td>
<td>tetraphenylporphyrinato anion</td>
</tr>
<tr>
<td>TS</td>
<td>transition state</td>
</tr>
<tr>
<td>TsOH</td>
<td>para-toluenesulfonic acid</td>
</tr>
<tr>
<td>Tyr</td>
<td>tyrosine</td>
</tr>
<tr>
<td>VA</td>
<td>vinylacetylene monomer; vinyl acetate</td>
</tr>
<tr>
<td>VC</td>
<td>vinyl chloride (1-chloroethylene)</td>
</tr>
<tr>
<td>VD</td>
<td>2-vinyl-1,4-dioxane</td>
</tr>
<tr>
<td>VDC</td>
<td>vinylidene chloride (1,1-dichloroethylene)</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>Ep</td>
<td>epoxide</td>
</tr>
<tr>
<td>Tol</td>
<td>toluene</td>
</tr>
<tr>
<td>$X_i$</td>
<td>intermediate species (intermediates)</td>
</tr>
</tbody>
</table>
In recent years, many books have appeared that are devoted to catalysis – a central, unifying concept in chemistry, including the rapidly developing homogeneous catalysis with metal complexes. This type of catalysis has demonstrated impressive achievements in synthetic organic chemistry and commercial chemical technology.

A reader might be surprised that yet another monograph on catalysis is offered to his or her attention. However, an unbounded field of knowledge such as catalytic chemistry can be considered in various aspects. The present book is aimed at providing a notion about the state-of-the-art in the theory of mechanisms of catalytic reactions in solutions, the state and possibilities of the kinetic method of investigation of the mechanisms of reactions involving metal complexes, a relationship between mechanistic hypotheses and existing kinetic models, and the kinetic models and mechanisms of many homogeneous catalytic processes employed in synthetic and commercial chemistry. Considerable attention in this monograph is devoted to the development of a rational strategy for kinetic models design, to the introduction of new concepts, and to an analysis of problems that are encountered in catalysis with metal complexes (including catalysis with nanoclusters and colloidal particles, homogeneity and heterogeneity of active catalysts, polyfunctional homogeneous catalytic systems, mechanisms of formation and decay of the active centers, chain mechanisms in the catalytic chemistry, allowance for a nonideal character of reaction media, etc.).

The Russian school of chemical kinetics has gained the respect of the world scientific community. It will suffice to mention only works by the Nobel Prize winner N.N. Semenov and other well known scientists such as N.M. Emmanuel’, M.I. Temkin, S.Z. Roginskii, G.K. Boreskov, I.I. Moiseev, A.E. Shilov, A.M. Zhabotinskii, S.L. Kiperman, G.S. Yablonskii and A.Ya. Rozovskii. On the other hand, for many reasons, the works of Russian scientists in chemical kinetics (as well as in other fields) only began to regularly appear in international editions in the last 20–25 years. This monograph, generalizing the main results obtained in the field of kinetics and mechanisms of homogeneous catalytic reactions involving metal complexes for the last 60 years, naturally also presents the most interesting investigations performed both in the former USSR and modern Russia.

The author is pleased to know that this book is now available to the whole catalytic community, rather than to Russian-speaking readers only, and is highly grateful to John Wiley & Sons for deciding to publish the English translation of his most recent monograph. This book is a combination of a scientific monograph and a handbook, and the author hopes that it will be useful to specialists as well as to advanced students, graduates, and postgraduates of universities and higher technology colleges by providing a deeper insight into catalytic chemistry, theory of reaction mechanisms, and chemical kinetics of homogeneous catalytic processes.

It is a great pleasure for the author to express his gratitude to Dr P. P. Pozdeev, the translator, for his kind consent to translate this huge monograph from the Russian, creative approach to this work, and fruitful cooperation in all stages of translation manuscript preparation.

O. N. TEMKIN
Preface

This book is an attempt to summarize the results of an approximately 60 year-long period in which the kinetic method was applied to investigations of the mechanisms of homogeneous catalytic reactions catalyzed by metal complexes. This period of time simultaneously featured both the establishment of homogeneous catalysis with metal complexes as one of the most important directions in catalytic chemistry and the development of a kinetic method and the corresponding approach to studying reaction mechanisms and constructing kinetic models of catalytic processes.

The theory of mechanisms of homogeneous catalytic reactions, including an analysis of the results of investigations of the structure of intermediates and the possible ways to their formation and transformation, noticeably outstrips possibilities of the experimental identification of the mechanisms of particular catalytic processes. Indeed, at the beginning of the 1950s, it was difficult to formulate even a single non-contradictory hypothesis concerning a possible mechanism of one or another catalytic reaction, whereas now the topical problem is how to perform discrimination of numerous probable, theoretically justified hypotheses. Both possibilities and limitations of the kinetic method have become evident. Consideration of the entire set of questions related to the kinetic aspects of homogeneous catalysis with metal complexes is the subject of this monograph.

Despite the great significance of catalysis with metal complexes in both commercial chemistry and organic synthesis, peculiarities and problems in the kinetics of homogeneous catalytic reactions in solutions of metal complexes – in contrast to the kinetics of gas-phase, enzymatic, and heterogeneous catalytic and topochemical reactions – are inadequately reflected in both basic monographs and teaching handbooks.

An analysis of the available literature, including monographs on separate types of catalytic reactions, and his own half-a-century experience led the author to the conclusion that writing a special monograph on the kinetics of catalytic reactions with metal complexes is expedient. This book presents a generalization of the results of studying the kinetics of various homogeneous catalytic (and, in some cases, noncatalytic) processes, which have been obtained since the beginning of 1950s for the reactions in solutions of both transition and nontransition metal complexes.

Traditionally, the kinetics of complex chemical reactions was developed within the framework of adjacent disciplines such as physical chemistry, chemical physics, and biophysics. Modern chemical kinetics can also be considered as a direction in the rapidly developing faculty of mathematical chemistry. Indeed, the direction in mathematical chemistry devoted to the kinetics analyzes the structure and dynamic properties of some special types of differential and algebraic equations. The first issue of a special international journal devoted to mathematical chemistry (Journal of Mathematical Chemistry) was published in 1987.

It is conventional that chemists employ the kinetic method for studying the reaction mechanisms, whereas mathematicians are engaged to solve the inverse problem of chemical kinetics (i.e., to estimate rate constants and parameters of kinetic models and assess the possibility of their identification), analyze the dynamical behavior of the system of differential equations, etc. The optimum situation would naturally imply a collaboration of chemists and mathematicians but, as the author’s experience shows, their effective cooperation is hardly possible for many reasons. In this context, one of the author’s goals is to concisely present in this book, intended mostly for chemists, the main mathematical approaches, ideas and problems that are important to understand when setting a kinetic experiment, discriminating hypotheses,
and interpreting kinetic data. It is hoped that this book will also suggest interesting research objects to specialists engaged in numerical simulations and mathematical chemistry.

The monograph considers the potential, achievements, and limitations of applying the kinetic approach to the identification of mechanisms of complex reactions and dwells on the issues of a rational strategy in constructing theoretically justified kinetic models. The kinetics of reactions in systems with associates and polynuclear complexes of metals is considered in detail. Factors that account for a multi-route character and a relationship between the topological structure of mechanisms and features of kinetic models are analyzed. The problem of kinetic and thermodynamic conjugation in complex reaction kinetics is discussed. Information on the basic principles and specific features of the dynamic behavior of nonlinear kinetic models (including mechanisms of oscillatory reactions) is presented and the thermodynamic, chemical, and mathematical principles of nonlinear dynamics are considered. In addition to data on the mechanisms of well-known processes such as the Belousov–Zhabotinski reactions, the book presents the results of studying the oscillatory reactions of oxidative carbonylation of alkynes in solutions of palladium complexes, which were discovered in the Department of Chemistry and Technology of Basic Organic Synthesis at the M.V. Lomonosov Moscow State University of Fine Chemical Technology, in the Laboratory of Kinetics and Catalysis headed by the author. The monograph briefly considers existing notions about the influence of a reaction medium and a nonideal character of the solutions of electrolytes and metal complexes in aqueous and nonaqueous media on the kinetics of reactions and the equilibrium of complex formation processes. Approaches to the elimination or allowance for these effects in setting kinetic experiments for the discrimination of hypotheses are discussed.

All sections of this book contain the results of original investigations that have not been considered previously in scientific monographs or teaching handbooks. In Chapters 1, 6, and 8, significant emphasis is placed on teaching aspects, whereas Chapters 2–5 and 7 mostly tend towards a scientific research character, although they can also serve as an additional teaching guide for advanced students, graduates, postgraduates and young specialists engaged in catalysis with metal complexes, complex reaction kinetics, and the theory of mechanisms of catalytic reactions.

O. N. Temkin
Acknowledgments

For my interest in catalysis with metal complexes, catalytic chemistry of alkynes, and kinetic methods of investigation, I am greatly indebted to Professor R. M. Flid – my teacher and friend for 20 years (1954–1974). Professor Flid was a student of Professor M.I. Usanovich (academician of the Kazakh Academy of Sciences) and Professor M.Ya. Kagan, and my meetings with Professor Usanovich for 18 years were an important school that significantly influenced my chemical outlook (see collection of memories Vospominaniya o Professore R.M. Flide [Remembering Professor R.M. Flid], Ekonomika, Moscow, 2006).

I am pleased to heartily express my acknowledgement to Professor I.I. Moiseev, academician of the Russian Academy of Sciences, for highly fruitful and stimulating contacts over more than 50 years.


I would like to express my deep gratitude to all of them.

I would like to thank S.M. Brailovskii for kindly permitting the use (in Chapters 1–3) of some materials from our manuscript, written in cooperation (1974) but yet unpublished, devoted to the kinetics of reactions in catalysis with metal complexes and to B.M. Mykhalichko and M.G. Mys’kin for kindly permitting the use of materials from our joint review on polynuclear copper(I) complexes.

I would like to gratefully mention E.D. German, my first supervised diploma student and friend, for that work marked the beginning of potentiometric investigations in situ for catalytic reactions in solutions of Cu(I, II), Ag(I), Hg(II), and Pd(I, II) complexes.

I am also heartily grateful to L.G. Bruk – my student, colleague and friend – for permanent and highly fruitful discussions of all aspects related to catalysis with metal complexes and the entire content of this monograph.

I would like to thank Yu.A. Pisarenko, N.B. Librovich, I.S. Kislina, and A.V. Zeigarnik for kindly reading separate chapters of this book and making highly valuable remarks, and to A.V. Kulik and A.P. Ivanov for their help in preparing the manuscript.

I would like to express my gratitude to D.K. Novikova, editor of the book, for her informal, constructive, and kind cooperation in carrying out a huge work on the manuscript preparation.

Finally, I am grateful to the Russian Foundation for Basic Research for financial support to publishing this book.

O. N. Temkin
About the Author

O. N. Temkin, the author of the monograph Homogeneous Catalysis with Metal Complexes: Kinetic Aspects and Mechanisms, is a well-known specialist in the field of chemical kinetics, catalysis with metal complexes, chemistry of alkynes, and mathematical chemistry. He is a professor of the M.V. Lomonosov Moscow State Institute of Fine Chemical Technology (now the M.V. Lomonosov Moscow State University of Fine Chemical Technology).

Professor Temkin is the co-author of three monographs and two chapters in monographs:


Professor Temkin designed for the first time kinetic models of numerous catalytic reactions of alkynes in superconcentrated Cu(I) chloride complex solutions, kinetic models of oxidation, oxidative carbonylation, and chlorination reactions of olefins, dienes, alkynes, and alcohols. He established catalytic systems for the anti-Markovnikov addition of water and hydrogen chloride molecules to alkynes, developed the catalytic chemistry of Pd(I) complexes, discovered a new type of oscillatory reaction in Pd-catalyzed carbonylation of alkynes and many other catalytic systems, and reactions catalyzed by metal complexes.
Introduction

The second half of the 20th century was marked in catalytic chemistry by an extensive development and effective use of catalysts based on metal complexes for homogeneous processes in chemical industry [1–7]. Since then, metal complex catalysts have become an important tool in modern synthetic organic chemistry [8–12], while their investigation provided a basis for ideas concerning the mechanisms of reactions in heterogeneous catalysis [13–16]. Academician I.I. Moiseev pointed out that “catalysis with metal complexes is an integral part of the scientific-technological revolution in the 20th century” [17].

At the end of the 19th century – i.e., much later than when K.S. Kirchhoff carried out his works on the acid catalysis of potato starch hydrolysis (1811) – three new directions were established in homogeneous catalysis [18, 19]. The use of aluminum complexes as catalysts for the alkylation and acylation of aromatic compounds by Ch. Friedel and J.M. Crafts in 1887 initiated the development of homogeneous electrophilic aprotic catalysis (AlCl₃, SnCl₄, SbCl₅, FeCl₃, etc.). A boost to investigations into the reduction–oxidation (redox) reactions with the participation of H₂O₂ and ROOH catalyzed by metal complexes was provided in 1894 by the work of G.J. Fenton on the oxidation of tartaric acid by dihydroperoxide in Fe(II) salt solution (now known as the Fenton reaction and reagent).

In continuation of the works performed by E. Linnemann, K.M. Zaitsev, and G.N. Glinskii in 1866–1867 [20], which discovered the hydrolysis of propenyl bromide and vinyl bromide in the presence of mercury acetate via the following scheme:

\[ \text{CH}_2=\text{CHBr} + \text{H}_2\text{O} \xrightarrow{\text{Hg(II)}} \text{CH}_3\text{CHO} + \text{HBr}, \]

M.G. Kucherov (Kutscheroff) in 1881 suggested that the formation of carbonyl compounds in this reaction is due to the elimination of HBr from alkenyl bromide and the addition of H₂O to the intermediate alkyne. Although Kucherov’s hypothesis was incorrect, the idea that Hg(II) salts catalyze the hydration of alkynes was successfully confirmed. This discovery, having drawn considerable interest from commercial chemistry, together with the aforementioned works by Linnemann, Zaitsev, and Glinskii, can be considered as triggering the development of the catalysis of organic reactions by complexes of post-transition (Cu, Ag, Au, Hg) and transition metals, involving the formation of organometallic intermediate compounds.¹ Subsequently, it was demonstrated that Hg(II) complexes possess the properties of typical aprotic acids and exhibit some features characteristic of platinum-group metals. The method of acetaldehyde synthesis was patented in 1910 (one year before the death of Kucherov), while the first commercial production

¹It should be noted that 2011 marks the 100th anniversary of the death of M.G. Kucherov, the well-known Russian scientist, and the founder of the catalysis with metal complexes.
of acetaldehyde via the Kucherov reaction was launched in Germany and Canada in 1916. At the same time, it was found by F. Klatte in 1913 that mercury salts in solution are capable of catalyzing the addition of acetic acid to acetylene with the formation of vinyl acetate and ethyldiene diacetate, and the addition of HCl to acetylene with the formation of vinyl chloride [21].

In 1929–1931, the American chemist, J. Nieuwland, discovered that copper halides catalyze the reactions of acetylene dimerization and trimerization [21]. The dimerization reaction scheme

\[
2\text{C}_2\text{H}_2 \xrightarrow{\text{Cu(I)}} \text{CH}_2=\text{CHC}≡\text{CH}
\]

provided a basis for the commercial synthesis of chloroprene as

\[
\text{C}_4\text{H}_4 + \text{HCl} \xrightarrow{\text{Cu(I)}} \text{CH}_2=\text{C(Cl)CH}=\text{CH}_2,
\]

and the related production of synthetic rubber as Neoprene (United States) and Sovprene (USSR). A significant contribution to investigations of this process and the development of chloroprene-based synthetic rubber technology was made by W. Carothers (USA) and A.L. Klebanskii (USSR). Copper(I) complexes also proved to be catalytically active in the hydrochlorination and hydration of acetylene. A “non-mercury” catalyst (CuCl–ZnCl₂–H₂O) of acetylene hydration (proposed in 1958) was comparable with the Kucherov catalyst in the activity, but significantly exceeded it with respect to stability [22]. In 1929, Nieuwland discovered the reaction of oxidative chlorination of acetylene to trans-1,2-dichloroethylene in the CuCl–CuCl₂–H₂O system. Somewhat later (in 1939), P. Kurtz established in Germany that the Nieuwland catalyst (CuCl–MCl–HCl–H₂O) was also active in the hydrocyanation of acetylene according to the following scheme:

\[
\text{C}_2\text{H}_2 + \text{HCN} \xrightarrow{\text{Cu(I)}} \text{CH}_2=\text{CHCN},
\]

which was used in 1942 by IG Farbenindustrie for the production of acrylonitrile.

Copper(I) complexes in solution were the first homogeneous catalysts of H₂ activation in the reactions of reduction of inorganic oxidizers and hydrogenation of \( p \)-benzoquinone (originally proposed by M. Calvin in 1938) [23]. In 1939, M. Iguchi discovered that rhodium complexes exhibited catalytic activity in the reaction of fumaric acid hydrogenation.

In the course of investigation of the hydrocarbon synthesis via the Fischer–Tropsch process on a CoTh/SiO₂ heterogeneous catalyst, O. Roelen in 1938 revealed a very interesting reaction of hydroformylation of olefins:

\[
\text{C}_2\text{H}_4 + \text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CHO}.
\]

It should be noted that Roelen at that time believed that the mechanism of this reaction included the formation of HCo(CO)₆.² In 1951, D.M. Rudkovskii with co-workers showed that this process (oxosynthesis) is homogeneous and can be catalyzed by cobalt carbonyl complexes [24]. Somewhat later, this was confirmed by I. Wender, G. Sternberg and M. Orchin [23]. As a result, Co₂(CO)₉ was introduced as the new type of catalyst into commercial catalysis with metal complexes.

Investigations of the reactions of carbon oxide with olefins, acetylene, and alcohols were carried out by W. Reppe from 1938 to 1945 (the results had become known only after World War II) and continued from 1951 to 1957 by the BASF company. Reppe with co-workers discovered several important catalytic reactions, including the carbonylation of methanol in solutions of Co, Ni, and Fe complexes,

\[
\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH},
\]

the hydrocarboxylation and hydrocarbalcoxylation of acetylene and olefins in solutions of Ni(0) and Ni(II) complexes,

\[
\begin{align*}
C_2H_2 + CO + ROH & \rightarrow CH_2=\text{CHCOOR (R–H, alkyl)}; \\
C_2H_4 + CO + ROH & \rightarrow CH_3CH_2COOR (R–H, alkyl),
\end{align*}
\]

and the cyclotrimerization \((C_6H_6)\) and cyclotetramerization \((C_8H_8)\) of acetylene (and alkynes) in nickel cyanide solutions in tetrahydrofuran. Thus, nickel and iron complexes were introduced into homogeneous catalysis with metal complexes. Reppe with co-workers also developed an original heterogeneous liquid-phase synthesis of 2-butyn-1,4-diol:

\[
C_2H_2 + 2CH_2O \rightarrow HOCH_2C≡CH_2OH,
\]

which was catalyzed by an organometallic compound \((\text{Cu}_2\text{C}_2\) supported on silica \((\text{Cu}_2\text{C}_2/\text{SiO}_2)\) obtained from \(\text{CuO}_2/\text{SiO}_2\). All these reactions (known as Reppe’s chemistry) became commercial processes. In particular, in 1948 Rohm & Haas Co. (USA) launched the synthesis of acrylic acid esters in \(\text{Ni(CO)}_4\) solutions, and BASF (FRG) in 1952 developed the production of propionic acid.

On the whole, twelve commercial processes using metal complexes were used in commercial chemistry in the middle of the 20th century. It is also interesting to note that it was Reppe who originally (in 1948) introduced phosphine ligands into practical catalysis with metal complexes. In particular, he established that \(\text{Ni(CO)}_2(\text{PPh}_3)_2\) exhibited very high activity in the oligomerization of acetylenes and \(\text{NiBr}_2(\text{PPh}_3)_2\) – in the synthesis of acrylates from acetylene.

Thus, at the end of the first stage in the development of catalysis with metal complexes, which terminated after World War II (at the end of the 1940s), investigations of the reactions catalyzed by metal complexes in solution were carried out mostly by industrial companies. The discoveries of Kucherov, Klatte, Nieuwland, Roelen, and especially Reppe had drawn the interest of chemical companies to the homogeneous catalysis with metal complexes, and this interest considerably increased after the new discoveries made in the 1950s to the 1970s. However, the academic community did not consider the development of new catalysts and processes as an independent direction in catalytic chemistry. In the first half of the 20th century, scientific research laboratories studied the catalysis of redox type reactions (e.g., reactions of hydrogen peroxide in solutions of metal ions and complexes, catalysis of the oxidation of metal ions and organic compounds) and modeled the catalase and peroxidase functions of enzymes. In particular, Shpitalskii [25] developed the first theory of intermediate compounds in homogeneous catalysis with metal complexes, which was based on the results of studying the kinetics of the catalytic decomposition of \(\text{H}_2\text{O}_2\). The proposed theory was used by F. Haber and J. Weiss in 1934 to develop a mechanism of this reaction in the Fenton system. Extensive research was also devoted to reactions in which metal ions and complexes played the role of electrophilic catalysts (Lewis acids) [23], including the hydrolysis of esters, amides, and phosphoric acid ethers, and reactions of decarboxylation, transamination, epoxide polymerization, aldol condensation, bromination, etc. Investigations of that period were summarized Langenbeck’s 1948 monograph [26] (with additional author’s comments and a bibliography extended to 1959 in the Russian edition of 1961), reviews of Baxendale [27] and Weiss [28], and monographs by Hein [29], Reppe [30], and Copenhaver and Bigelow [31]. At the First International Congress on Catalysis that was held in 1956 [32], five reports were devoted to the homogeneous catalysis with metal complexes in reactions of hydrogenation and reduction, oxidation, hydroformylation, isomerization, and hydrocyanation of olefins.

The role of \(\pi\)- and \(\sigma\)-organometallic intermediates in the catalysis of organic reactions by metal complexes was not understood at the first stage of development of the catalysis with metal complexes. Although Kucherov tried to isolate and study the proposed organomercuric compounds in the reaction of acetylene hydration, Nieuwland and Kleibanskii considered \(\text{trans-}\beta\)-chlorovinylmercury chloride (\(\text{ClHgCH=CHCl,}\)
Biginelli complex) formed from mercuric chloride and acetylene (as was known from 1898 [22]) and the product of acetylene insertion into the Hg–OH bond as intermediates in the reactions of acetylene hydrochlorination and hydration (see, e.g., [33]), and the first organocopper products of the interaction of C₂H₂ and CuCl were originally synthesized as long ago as 1900 [22]. Apparently, the role of organometallic intermediates was most adequately recognized by Yu.S. Zal’kind and B.M. Fundyler in 1936, when it was shown that the stoichiometric oxidation of Cu(I) acetylides (known as the Glaser reaction since 1869 [22]) could be implemented for the catalytic oxidative coupling of alkynes by combining the reactions of acetylide formation and oxidation in a common system (Glaser–Zal’kind reaction) as

\[
2\text{RC}=\text{Cu} + \text{Ox} \rightarrow \text{RC}=\text{CC}=\text{CR} + \text{Red} + 2\text{H}^+.
\]

\[(\text{Ox}=\text{O}_2, \text{Fe}^{3+}, \text{Cu}^{2+})\]

The situation in the homogeneous catalysis with metal complexes dramatically changed as a result of a series of discoveries made and investigations performed by academic scientists in cooperation with industrial companies in the period from the beginning of 1950s up to 1961–1963. This period can be considered as the second stage in the development of the catalysis with metal complexes. The following investigations performed at that time in the fields of organometallic, coordination, and catalytic chemistry were of key importance for the subsequent rapid progress in the catalysis with metal complexes.

(i) Immediately after the synthesis of ferrocene \((\text{C}_5\text{H}_5)_2\text{Fe}\) in 1952, J. Wilkinson, R. Woodward and E. Fischer explained the structure of this organometallic compound, and then (in 1955) Fischer synthetized a no less remarkable complex of \((\text{C}_6\text{H}_6)_2\text{Cr}\). These events marked the onset of the systematic development of the organoelemental chemistry of transition metals and the theory of the structure of \(\pi\) complexes of transition metals. For these works, G. Wilkinson and E. Fischer received the Nobel Prize for Chemistry in 1973.

(ii) In 1953–1955, K. Ziegler and G. Natta proposed the heterogeneous (and then, homogeneous) organometallic catalysts for the stereoregular polymerization of \(\alpha\)-olefins and dienes (\(\text{TiCl}_4–\text{AlEt}_3\), \(\text{TiCl}_3–\text{AlR}_3\), \((\text{C}_5\text{H}_5)_2\text{TiCl}_2–\text{Al}(\text{C}_2\text{H}_5)_3\), etc.). In 1963, these scientists were awarded the Nobel Prize for creating a new approach to the chemistry and technology of polymers. The results of investigations into the polymerization of olefins and dienes, which were performed at the second stage of development of the catalysis with metal complexes, were summarized by Gaylord and Mark [34].

Investigations of the \(\text{NiX}_2–\text{AlR}_3\) system, which led to the discovery of Ziegler’s catalysts (or the so-called “nickel effect”), provided a basis for the development of the commercial technologies of olefin dimerization and diene cyclooligomerization (G. Wilke) and the creation of the catalytic chemistry of Ni(0) complexes and bis-\(\pi\)-allyl Ni(II) complexes.

(iii) In 1959–1960, J. Smidt and W. Hafner with coworkers in Germany as well as I.I. Moiseev, M.N. Vargaftik, and Ya.K. Syrkin in the USSR reported on the discovery of a new type of catalytic reactions for olefin oxidation in solutions of \(\text{Pd}(\text{II})\) complexes, in particular,

\[
\text{C}_2\text{H}_4 + \frac{1}{2}\text{O}_2 \xrightarrow{\text{PdCl}_2–\text{CuCl}_2} \text{CH}_3\text{CHO}.
\]

\(^3\)The first patent application that described a gas-phase reaction on carbon-supported \(\text{PdCl}_2–\text{CuCl}_2\) catalyst was submitted in January 1957 (see R. Jira, \textit{Angew. Chem. Int. Ed.}, \textbf{48}, 9034 (2009)).