Preface

A radical is any molecule or atom which possesses one unpaired electron. Radicals are of great importance since they often appear as intermediates in thermal, radiation, and photochemical reactions. It is noteworthy that radicals are usually produced in pairs through the above-mentioned reactions. Such a pair of radicals has been called "a radical pair". Thus, radicals and radical pairs play very important roles in chemical and biochemical reactions. For example, they appear in such important processes as polymerisation and combustion reactions, radiation curing and lithography, photosynthesis in plants and bacteria, autooxidation and aging of organic molecules, polymers, and living organisms, and stratospheric ozone depletion by freons. This is a book about reaction dynamics of radicals and radical pairs in the presence and absence of an external magnetic field and its applications to many related phenomena in chemistry, physics, and biology. It grew out of a lecture which was given every year from 1997 to 2001 by the author to the Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology.

Electron Spin Resonance (ESR) or Electron Paramagnetic Resonance (EPR) is one of the most powerful methods for investigating the structure and reaction dynamics of radicals and radical pairs. In ESR experiments, an external magnetic field is applied to radicals and radical pairs, which are split into their individual spin sub-levels by the field. A resonance microwave is also applied to them and induces the transitions between their individual spin sub-levels. At first, most ESR measurements were carried out under steady-state conditions because usual ESR apparatus adopted 100 kHz field-modulation in order to improve their sensitivity. This means that the time resolution of such measurements with field-modulation should be longer than 0.1 ms. Afterwards, ESR measurements were also made during chemical reactions with much shorter time resolutions of up to 10 ns. The intensities of ESR spectra of some reacting systems were found to show emission and/or enhanced absorption, but other characteristics such as line frequencies and line width to be normal. Such peculiar ESR signals have been called "Chemically Induced Dynamic Electron Polarization (CIDEP)". Similar anomalous signals were also observed for nuclear magnetic resonance (NMR) spectra when they were measured during chemical reactions and have been called "Chemically Induced Dynamic Nuclear Polarization (CIDNP)".

CIDEP and CIDNP are due to nonequilibrium populations in the electron spin sub-levels of reacting radicals and in the nuclear spin sub-levels of reaction products, respectively. CIDEP and CIDNP have been successfully explained by the radical pair mechanism, according to which the singlet and triplet states of radical pairs can be mixed with each other through the Zeeman interaction

between radicals and the external magnetic field and the hyperfine interaction between electron and nuclear spins inside the radical pairs. Because the populations of electron and nuclear spin sub-levels can be changed by ordinary magnetic fields through the radical pair mechanism, not only the yield of reaction products generated through radical pairs but also the reaction rates of radical pairs were also expected to be affected by the fields. Indeed, such effects have been observed for many chemical and biochemical reactions through radical pair, being called "Magnetic Field Effects (MFEs)" upon chemical reactions.

Discoveries of CIDEP, CIDNP, and MFEs in chemical reactions through radical pairs brought about the advent of a new research field, which has been called "Dynamic Spin Chemistry". Dynamic spin chemistry encompasses not only basic theoretical and experimental investigations of all phenomena in which free radicals and other species possessing unpaired electron spins occur but also many important applied researches including photosynthesis in plants, biochemical reactions in human and animal bodies, and various industrial processes. Let us show two interesting problems concerning MFEs on biological processes. The homing of pigeons has been considered to be due to a magnetic compass inside the brain of pigeons. There have been many scientific papers reporting that environmental electromagnetic radiation causes children cancer. In my opinion, these two important phenomena have neither been proven by reproducible experiments nor been explained by reliable theories. Many interesting problems including the above-mentioned ones have been left for further investigations of dynamic spin chemistry in the 21st century. Because the radical pair mechanism is well understood and based on established science, I can say that dynamic spin chemistry provides a good guidance for researchers of MFEs on biological processes as well as other processes.

This is not the first book on CIDEP, CIDNP, and MFEs in chemical and biochemical reactions, but most of the other books were written for specialists of dynamic spin chemistry without explaining how to derive its basic principles. This book differs from others in the emphasis placed on making it a learning text for those with minimum knowledge in quantum mechanics. At the same time, this text serves a secondary purpose of showing how the field of dynamic spin chemistry has been established from a veil of secrecy, historically important papers being introduced to the beginners of this field. The first half of this book explains the basic principles in magnetic properties of electron and nuclear spins, ESR and NMR, the radical pair mechanism, CIDNP, CIDEP, and MFEs upon chemical reactions due to the radical pair mechanism. The second half describes typical results on dynamic spin chemistry, including MFEs due to the relaxation mechanism, MFEs on chemical reactions through biradicals, magnetic isotope effects, triplet mechanism, theoretical analysis of dynamic spin chemistry, effects

of ultra-high magnetic fields upon chemical reactions, MFEs on chemical reactions through high spin species, optical detected ESR and reaction yield detected ESR and MFEs upon biochemical reactions and biochemical processes.

I hope that this book will be useful not only for graduate and senior undergraduate students of pure and applied chemistry, physics, and biology but also for academic and industrial researchers in the fields of dynamic spin chemistry, photochemistry, photophysics, photobiology, magnetic resonance, electromagnetism, environmental science and nano-scale technologies.

The author expresses his sincere thanks to Prof. Saburo Nagakura, President of Kanagawa Academy of Science and Technology, for his encouraging the author to write this book, to Prof. Sheng Hsien Lin, President of Institute of Atomic and Molecular Sciences, for his inviting the author to publish this book at World Scientific Publishing Company, and to the editors of World Scientific Publishing Company for their editorial efforts. The author is also thankful to those publishers which kindly permitted him to use their figures and tables in this book.

Tokyo, January 2003 Hisaharu Hayashi