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Book review

Dynamic spin chemistry. Magnetic controls and spin dynamics of chemical reactions. Saburo Nagakura, Hisaharu Hayashi and Tohru Azumi (Eds.), Kodansha and Wiley, 1999; 299 + xiii pp., ISBN Kodansha: 4-06-209180-1; Wiley: 0-471-32836-7.

The term of 'magnetic field effect' (MFE) always arouses my interest, because I started to examine MFE with colleagues on photolysis of dibenzoyl peroxide in early 1970s and then wrote a short review on MFE; furthermore, there seem many phenomena effected by magnetic field (MF) such as flying of bees and pigeons sensing very weak MF of the Earth.

Organic free radical reactions have long been supposed to suffer effect of paramagnetic species or MF. In Japan in late 1930s Urushibara et al. examined effect of paramagnetic metals on newly found free radical addition reactions. J.E. Leffler, who attempted pioneering work to conduct organic free radical reactions including radical polymerization in a magnet (0.75 T) soon after the second world war (1949), described the status of those days in his book 'The reactive intermediates in organic chemistry' (Interscience Publishers, New York, 1956) that paramagnetic effect had not been demonstrated unambiguously to affect the rate of free radical reactions.

Since late 1960s, however, MFE began to be investigated again in the areas of electrogenerated chemiluminescence, photochemical and thermal reactions as well as radiation-induced polymerization, mostly owing to progress of analytical tools and later stimulated by discovery of chemically induced dynamic nuclear polarization (CIDNP). The situation of those days was described in reviews published in 1970s: my short review [Kagaku (Chemistry) 30 (1975) 326] and those of P.W. Atkins [Chem. Brit. (1976) 214; Ann. Rep. Chem. Soc. A65 (1975) 67] and Yu. Molin [Sov. Sci. Rev. B. Chem. Rev. 1 (1979) 1].

Since then superconducting magnets became available to examine MFE up to several T. This enabled us to reveal MFE further, which had not been so clearly detected at lower MF. The results of MFE started to provide more insight into the nature of radical pairs to elucidate mechanism of free radical reactions and spin polarization. However, as far as the yields of final reaction products were concerned, MF certainly changed their composition but not in such a drastic way as to be used for synthetic purpose. Later, use of transient spectroscopy has revealed that the yields or lifetimes of intermediate radicals or exciplexes can suffer MFE more remarkably than the yields of final reaction products.

Research on MFE may often be carried out in ambitious atmosphere expecting discovery of novel phenomena. Probably because of this atmosphere, there have long been not a few number of reports with unreproducible results even in the middle of 1990s. Some of them looked suspicious from the beginning. This may not only arise from overambitiousness of workers but also from poor performance of tools for separation, purification and determination of compounds in former days and perhaps lack of appropriate experimental skills in preparative works on organic compounds even with specific configuration.

The present book is contributed by 11 Japanese scientists who joined the research project called 'Molecular magnetism' carried out in 1992–1995 by the support of the Ministry of Education, Science and Culture. This book is composed of eight chapters. The first introductory chapter, 'What is dynamic spin chemistry?', was written by S. Nagakura, an internationally renowned leader in this field. Other seven chapters are roughly divided into two parts. The first part (chapters 2–5) is devoted to MFE on chemical reactions and equilibrium. The second part (chapters 6–8) depicts recent progress in spectroscopy for spin dynamics such as that for examining nuclear spin polarization, CIDEP for elucidation of mechanism of photochemical reactions, reaction-yield-detected EPR, and so on.

The first part describes MFE on various inter- and intra-molecular photochemical reactions in condensed phase with MF varying from very weak MF of mT to up to very strong MF of tens T, and argues the results based on the radical pair model. The MFE is generally enhanced in micelles due to increase of the lifetime of the resulted radical pairs. In intramolecular systems, MFE is quite strongly controlled by distance between the radical centres in biradicals. For example, MFE determined as ratios of absorbance for transient absorption of resulted radicals, intensities for emission or lifetimes of intermediate exciplex measured at an applied MF to those without applied MF attains to a value as large as more than 20 in some cases. Subsequently, description proceeds to precise analysis of behaviour of excited molecules in gas phase with respect to vibrational levels.

The second part of the book deals with various recent progress in spectroscopy to observe the behaviour of species

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carrying electron spins. Let me cite an example in elucidation of mechanism of photochemical reactions. On photolysis, generated radical pairs tend to diffuse from solvent cages to give escaped free radicals, and the paired and escaped radicals behave respectively. In the transient absorption, both the radicals show the same absorption but decay with different lifetimes. Time-resolved EPR can further reveal behaviours of these species. EPR signals of spin-correlated radical pairs (SCRP) and escaped radicals decay with different lifetimes each corresponding to those observed in transient absorption. Transient absorption determined under MF of a magnet decays with lifetimes different from those in the absence of MF due to change of extent of the intersystem crossing of the radical pairs under MF. Decay of EPR signals is also affected by intensities of microwave power applied.

In this book all chapters are contributed by experts and are harmonized as a whole, much owed to the editors. This book, therefore, offers valuable information on the research of MFE on chemical reactions and spin dynamics. Relatively small numbers of misprint should be corrected on an appropriate occasion.

Finally, it is to be noted that nowadays interest in MFE does not remain at chemical reactions but is further expanded to various phenomena. Moreover, a convenient type of magnet has become available, that is, a conduction cooled superconducting magnet carrying large cavity space and furthermore without need for supplying liquid helium. ‘New magneto-science’ is rapidly growing up as seen in recent publication of special issues of journals [Kagaku Kogyo (Chemical Industry) 48 (1997) 769–830; Nippon Kinzoku Gakkaishi (J. Jpn. Inst. Metals) 61 (1997) 1272–1340]. There are really many remarkable findings such as displacement of liquid surface by strong MF named as ‘Moses effect’ by K. Kitazawa [for example, Nature 393 (1998) 749], germination of plants such as cucumber controlled by strong MF for their growing direction [interesting pictures are shown in N. Hirota and K. Kitazawa, Gendai Kagaku (Chemistry Today), May 1999, 51], MFE on electrolysis due to magneto-hydrodynamic (MHD) effect [R. Aogaki et al., Physica B 201 (1994) 611], on combustion, particularly acceleration under gradient MF [N. Wakabayashi, Combustion and Flame 93 (1993) 207] and on crystal growth in addition to hitherto examined alignment of liquid crystals and crystalline polymer by MF. The present reviewer looks forward to learning further progress of research on MFE, which will reveal how MFE can appear in widely ranging phenomena and how it is controlled by the rule of Nature.

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