Developments of Magnetic-Resonance-Related Spin Chemistry in Japan

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Abstract. A review on the developments of the magnetic-resonance-related spin chemistry in Japan is presented. We describe how studies in this area started in Japan and developed into the flourishing state of the present. Important contributions made by Japanese spin chemists in the last two decades in three areas, namely, work on chemically induced dynamic electron polarization, excited states and controlling of photochemical reactions, are presented. More emphases are placed on the new developments in recent years, particularly new concepts and new methodologies.

1 Introduction

Spin chemistry may be defined as the area of the study of magnetic field and spin effects in chemistry. The magnetic resonance techniques, especially those related to electron paramagnetic resonance (EPR), play essential roles in spin chemistry. In Japan the research in the magnetic-resonance-related spin chemistry started around 1980, about ten years later than in the US and Europe, but it quickly became a popular field of research and is now flourishing with many new exciting developments. In this review we describe how these studies in Japan started and developed into the flourishing state of the present, by reviewing contributions by Japanese scientists in the last two decades. We start with a brief historical overview of these studies.

EPR studies in chemistry in Japan started in the late 1950s and quickly gained popularity as a new exciting research field. By the early 1960s there were already enough research activities to start an annual discussion meeting; in 1962 a group of young chemists organized the “Annual ESR (EPR) Symposium” sponsored by the Japanese Chemical Society to discuss research results and exchange ideas. Numerous interesting problems such as electronic and molecular struc-
tures of stable and unstable free radicals and their reaction dynamics were studied in those days, but the dynamics of the spin effects could not be studied directly by EPR because of the limited time resolution and sensitivity of the spectrometer. Consequently there was no concept of spin chemistry among the scientists involved in the early EPR studies. It was after the advent of the time-resolved EPR (TREPR) spectroscopy that the EPR technique became truly useful in spin chemistry.

Two observations relevant to the development of TREPR were made around 1970: CIDEP (chemically induced dynamic electron polarization) in photochemical reactions [1, 2] and spin polarization in organic triplets [3, 4]. These observations showed non-Boltzmann distributions among spin sublevels after photochemical reactions and creation of triplet states via intersystem crossing from excited singlet states, respectively. The fact that these processes could produce spin polarizations much larger (sometimes more than 100 times) than those obtained by the Boltzmann distribution was essential for the development of TREPR spectroscopy, since with this large spin polarization one could achieve high sensitivity in TREPR. Pioneering works on TREPR were made in the 1970s by McLauchlan [5], Trifunac [6], Fessenden [7], Weissman [8] and others. The direct detection method without magnetic field modulation was particularly useful in the TREPR spectroscopy on a continuous-wave (cw) EPR spectrometer. With the help of the large spin polarization obtained by pulsed laser excitation, the TREPR technique enabled one to follow spin dynamics directly with a time resolution of submicroseconds with good sensitivity. Following the developments of the pulsed EPR technique, TREPR experiments were also performed with pulsed EPR spectrometers [9]. The pulsed method has the obvious advantage that the time evolution of the spin system is not perturbed by the interaction with the microwaves.

In the middle of the 1970s Nagakura’s group started to study magnetic field effects (MFE) on chemical reactions [10]. They found MFE on chemical reactions in various systems and elucidated the mechanisms to produce MFE [11]. However, these studies developed studies independent of EPR at this stage. This was probably because their interest was mainly aimed at the investigation of electron and nuclear spins in a radical pair (RP) as a chemical intermediate. At that time an intermediate RP had not yet become the main target of an EPR study in Japan, although RPs had been studied by EPR in solid matrices [12, 13] and invoked in the interpretations of CIDEP [14, 15] and CIDNP (chemically induced dynamic nuclear polarization) [16] phenomena.

TREPR work in Japan started in the early 1980s. By this time considerable progress had been made in the TREPR spectroscopy in the US and Europe [9], but it was still possible to make many new interesting studies with TREPR. Obi and Murai made the first report on TREPR work on the triplet benzophenone [17] and biacetyl [18] in 1982, and Hirota and Yamauchi in 1983 [19] on the short-lived nonphosphorescent triplet states. Hayashi, who had been working on MFE, also started TREPR work in collaboration with Murai to study spin effects upon photochemical reactions. They studied the photochemical reaction of benzophenone in micelles in 1984 [20] and reported a peculiar lineshape of the spectrum,