Early days when we challenged the magnetic field effect on free radical reactions of organic peroxides

Katsumi Tokumaru^a Professor Emeritus of University of Tsukuba

Our intention to examine the effect of external magnetic field on free radical reactions of dibenzoyl peroxide in early 1970's and its background and subsequent story are described.

When I was a graduate student at University of Tokyo in middle 1950's, I worked with the late Prof. Osamu Simamura on mechanism of reactions of organic peroxides in solution. He contributed a lot to exploring a new field of organic free radical chemistry since his graduate student days working with the late Prof. Yoshiyuki Urushibara at University of Tokyo by revealing participation of free radicals in the so-called abnormal addition of hydrogen bromide to unsaturated bonds under the air, which occured in a completely different way from that of hydrogen chloride. They called this phenomenon as "oxygen effect".¹⁾ It was nearly the same time when Morris Kharasch and his coworkers discovered the essentially same phenomenon at Chicago and called it as "peroxide effect".²⁾ Moreover, Urushibara's group presumed that paramagnetic substance and external magnetic field would affect these free radical reactions, and examined the effect of added finely divided metallic nickel and iron³⁾ and further tried the reaction in a magnet, though not gaining any result.⁴⁾

As to the late Prof. Simamura, it was regrettable for us that we lost a chance to read his book describing his understanding of organic reaction mechanism soon after the WWII, because its final manuscript handed to a publisher was burnt by US Air bombardment to Tokyo in early summer 1945. After the war, his book was still listed in an anouncement of forthcoming books in a series of monographs of chemistry (Kagaku Syusyo) of the publisher;⁵⁾ in those days, however, one could not have copied a long manuscript. When I saw his hand-written seemingly pre-final manuscript after his passing away, I imagined how it would have encouraged us to read this in our student days.

I was grown up in such a laboratory. When I worked as a research associate in his laboratory in early 1960's, photochemistry began to attract much attention and convenient mercury lamps became available with reasonable prices. This led me to use these light sources to generate free radicals from initiators at ambient or low temperature and to shift my interest to photochemistry which enabled me to follow reaction courses in more dynamic way than in traditional "dark" reactions. We investigated photochemical decomposition of dibenzoyl peroxide (BPO), a very familiar compound for me and one of the most frequently used initiators of vinyl polymerization in industry. We found that both direct irradiation and singlet sensitization by aromatic polycyclic hydrocarbons such as chrysene produced phenyl benzoate as a geminate product between the initially resulted benzoyloxyl and phenyl radicals in addition to diffusion products arisen from reactions of free radicals with a solvent employed, but triplet sensitization very much suppressed formation of the geminate product.⁶⁾

In late 1960's, chemically induced dynamic nuclear polarization (CIDNP) was discovered by Bargon and Fischer and by Kaptein, and behaviours of the radical pair with spin multiplicity of either singlet or triplet pair and their interconversion induced by applied magnetic field became a target of active discussion.⁷⁾

In early 1970's, I got an idea to examine the effect of magnetic field on photolysis of dibenzoyl peroxide (BPO), since application of magnetic field will accerelate the conversion of spin multiplicity of the initially resulted radical pair and, therefore, will change the composition of the geminate and the diffusion products. For example, when singlet pairs of benzoyloxyl and phenyl radicals are initially produced, application of magnetic field would enhance its spin inversion to the triplet radical pairs, thus lowering the yield of the geminate product and enhancing those of the diffusion products, since these radicals have g-values of 2.010 and 2.002, respectively. Thus, I expected Zeeman effect will accelerate the conversion between their singlet and triplet radical pair.

Eventually in 1973, I was invited as a visiting scientist by Dr. Masaki Hasegawa (later Prof. at University of Tokyo) at Research Institute of Polymer and Textile at Yokohama (later National Institute of Materials and Chemical Research, NIMC, at Tsukuba and now National Institute of Advanced Industrial Science and Technology, AIST), who discovered very novel solid-phase photopolymerization of diacetylenic compounds at that time and was extending their work to various photochemical processes.

A JEOL electromanet was available in his laboratory. Dr. Hirochika Sakuragi (now Prof. at University of Tsukuba) and Ms. Tamako Mishima (now Prof. at Tokyo Kasei Gakuin Women's College) in our laboratory worked together with Drs. Masako Sakuragi and Syoji Watanabe there. We paid very careful attention to get reproducible results. On increase of magnetic field from 0 to 1.4 T, the highest value

^a Corresponding address: 1–5–10, Furu-ichiba, Saiwai-ku, Kawasaki, 212–0052 Japan

with that magnet, the product yields did not seem to show appreciable variation exceeding experimental error. However, when I looked at data plotting the geminate product yield against magnetic field, I felt in some runs the yield hopefully tended to increase at nearly 1.2 T. Occasionally, Dr. Peter Atkins, who was engaged in theoretical consideration of magnetic field effect on chemical reactions⁸⁾ at Oxford University, stayed at Tokyo in spring 1974 hosted by the late Prof. Katsunori Hijikata at the University of Electro-Communications. We had several occasions to discuss together.

I though it would be worthwhile to report our attempt, though not yet getting clear results, at a meeting ⁹⁾ and as a paper.¹⁰⁾ Dr. Hirochika Sakuragi presented our attempt at the Symposium on Photochemistry in 1974 at Nagoya. Prof. Saburo Nagakura at University of Tokyo and RIKEN at that time was among the audience and told me his interest in our approach aiming to enhance either geminate or diffusion reaction pathway by applying magnetic field.

In those days examination of magnetic field to chemical reactions was challanging but "dangerous" because of not gaining any fruit. I still recall very kind advise from one of my old friends that it would better for me not spend time in such a seemingly unpromising subject before getting a professor chair. A few weeks after the Symposium Prof. Nagakura called me to propose to reexamine our attempts using a superconducting magnet at RIKEN. Dr. Hirochika Sakuragi worked for preparation of the samples and gas chromatographic analysis of the reaction products, and Drs. Hisaharu Hayashi and Yoshifumi Tanimoto, who were staffs at Prof. Nagakura's laboratory, worked at RIKEN for irradiation in a superconducting magnet.

Application of magnetic field up to 4.3 T in a superconducting magnet gave clear results. Thus, as predicted before, increase of magnetic field on chrysene-sensitized irradiation of dibenzoyl peroxide in toluene at ambient temperature lowered the yield of the geminate product, phenyl benzoate, (decrease of 8% of the yield without magnetic field) and enhanced those of the diffusion products, methylbiphenyls and 1,2-diphenylethane (increase of 2% of their yields). This result clearly demonstrated acceleration of the interconversion of the initially resulted singlet radical pair to the triplet radical pair by the Zeeman effect.¹¹

Magnetic field effect on photolysis of dibenzoyl peroxide was further extended by Dr. Yoshio Sakaguchi working as a graduate student with Prof. Nagakura.¹²⁾

Meanwhile I had an occasion to publish a short article of 3.5 printed pages summarizing the status of the invesigation of magnetic field effect on chemical reactions in 1975.¹³⁾ During preparation of this article I was very much impressed to find that as early as in 1949 soon after the WWII the late Prof. John E. Leffler (at that time at Cornell University, later at Florida State University), who often presented important concepts and was the author of several well reputed books such as "The Rate and Equilibrium in Organic Reactions", tried magnetic field effect on thermal decomposition of dibenzoyl peroxide¹⁴⁾ and vinyl polymerization¹⁵⁾ at 0.75 T though not getting any positive result. He summarized the status in the middle 1950's in his book that paramagnetic effect had not been demonstrated unambigously to affect the rate of free radical reactions.¹⁶⁾

In 1976 I joined Japan-US Seminar on organic peroxides organized by the late Professors Shigeru Oae (University of Tsukuba) and Leffler at Colorado and discussed on these matter particularly with Professors Leffler and James McBride (Yale University). The latter organized the Gordon Conference on Organic Free Radical Chemistry in the next year (1977) and invited me to give a talk on photochemical reactions of dibenzoyl peroxide and the magnetic field effect.

During discussion on these occasions, I found there were many tasks to be examined in the magnetic field effect. Examination in a magnetic field of a superconductive magnet was carried out mostly for chrysene-sensitized decomposition of dibenzoyl peroxide in aromatic hydrocarbons. Effect on irradiation in different conditions and of various peroxides was worth to be examined. However, as to the extent of the magnetic field effect, decrease of the yield of the geminate product was very little, from nearly 10% at 0 T to nearly 9% at 4.3 T, which corresponded to nearly 8% reduction of the yield. Thus, the effect of high magnetic field on final products still remained at small extent and was far from controlling the reaction course by magnetic field.

To reveal the mechanism of photolysis of the peroxide, it was more important to work with time-resolved laser spectroscopy. One was time-resolved EPR with Professors Noboru Hirota and Seigo Yamauchi (now at Tohoku University) to identify generated free radicals and to determine their kinetic behaviours at their laboratory, Kyoto University.¹⁷⁾ The other was time-resolved transient absorption to follow absorption of benzoyloxyl radicals, in more general, aroyloxyl radicals generated from diaroyl peroxides of various structure.¹⁸⁾ These two procedures revealed that aroyloxyl radicals undergo decarboxylation or reactions with substrates with very wide range of rate constants. Mechanism of sensitization of peroxides and other radical initiators is still interesting subjet of active investigation especially for polymeric film system from viewpoint of developing new photorecording materials.¹⁹⁾

Regarding magnetic field effect, I regret not to make chance to examine magentic field effect on transient absorption of aroyloxyl and other radicals. Moreover, with recent development of magnets of very high field, I still wish to see the results of the above typical reaction in magnetic fields higher than 10 T, since the above reaction is one of a few cases showing participation of the Zeeman effect in the magnetic field effect.

References

- Their works in those days is summarized in Y. Urushibara: in Kagaku Soho, (in Japanese) Vol. 6, edited by Monbusho Kagaku Kenkyu Kaigi (Iwanami, Tokyo, 1944), p. 49. This volume is composed with other three contributions by J. Horiuti, S. Kawai, and K. Higashi.
- 2) M. S. Kharasch, H. Engelmann, and F. R. Mayo: J. Org. Chem. 2, 288 (1937). As a summarized article: F. R. Mayo: in Vistas in Free Radical Chemistry, edited by W. A. Waters (Pergamon Press, London, 1959), p. 139.
- Y. Urushibara and M. Takebayashi: Bull. Chem. Soc. Jpn. 11, 692 (1936); Y. Urushibara and M. Takebayashi: Bull. Chem. Soc. Jpn. 12, 51 (1937).
- M. Takebayashi, private communication; A. Sugimori and N. Inamoto: Kagaku to Kogyo (in Japanese) 45, 2044 (1992).
- 5) In an announcement of Kawade Syobo, Tokyo, in 1948, the following is seen: O. Simamura: Yuki Kagaku ni okeru Denshi Riron (Electronic Theory in Organic Chemistry) (in

Japanese). One of the well-read books in this series of monographs was T. Ogata: Kanko Shikiso to sono Oyo (Dye Sensitizers and their Application) (in Japanese) (Kawade Syobo, Tokyo, 1948).

- T. Nakata, K. Tokumaru, and O. Simamura: Tetrahedron Lett. **1967**, 3303; T. Nakata and K. Tokumaru: Bull. Chem. Soc. Jpn. **43**, 3315 (1970); K. Tokumaru, A. Ohshima, T. Nakata, H. Sakuragi, and T. Mishima: Chem. Lett. **1974**, 571; H. Kitamura, H. Sakuragi M. Yoshida, and K. Tokumaru: Bull. Chem. Soc. Jpn. **53**, 2413 (1980).
- For example: H. Fischer and J. Bargon: Acc. Chem. Res. 2, 110 (1969); R. Kaptein: Chem. Phys. Lett. 2, 261 (1968).
- As reviews: P. W. Atkins and T. P. Lambert: Ann. Rep. Chem. Soc. A 65, 67 (1975); P. W. Atkins: Chem. Br., 12 214 (1976).
- H. Sakuragi, T. Mishima, K. Tokumaru, M. Sakuragi, S. Watanabe, and M. Hasegawa: Abstracts of Symp. Photochemistry, Nagoya, 1974-10 (1974), p. 67.
- H. Sakuragi, M. Sakuragi, T. Mishima, S. Watanabe, M. Hasegawa, and K. Tokumaru: Chem. Lett. **1975**, 231.
- Y. Tanimoto, H. Hayashi, S. Nagakura, H. Sakuragi, and K. Tokumaru: Chem. Phys. Lett. 41, 267 (1976).

- 12) Y. Sakaguchi, H. Hayashi, and S. Nagakura: Bull. Chem. Soc. Jpn. 53, 39 (1980).
- K. Tokumaru: Kagaku (Chemistry) (in Japanese) 30, 326 (1975).
- 14) J. E. Leffler: J. Chem. Phys. 17, 741 (1949).
- 15) J. E. Leffler and M. J. Sienko: J. Chem. Phys. 17, 215 (1949).
 16) J. E. Leffler: in *The Reactive Intermediates in Organic*
- *Chemistry* (Interscience Publishers, New York, 1956), p. 249.
 S. Yamauchi, N. Hirota, S. Takahara, H. Sakuragi, and
- K. Tokumaru: J. Am. Chem. Soc. **107**, 5021 (1985); S. Yamauchi, N. Hirota, S. Takahara, H. Misawa, K. Sawabe, H. Sakuragi, and K. Tokumaru: J. Am. Chem. Soc. **111**, 4402 (1989).
- 18) H. Misawa, K. Sawabe, S. Takahara, H. Sakuragi, and K. Tokumaru: Chem. Lett. **1988**, 357; As a summarized paper: J. Wang, T. Tateno, H. Sakuragi, and K. Tokumaru: J. Photochem. Photobiol. A **92**, 53 (1995).
- For example: K. Tokumaru: Res. Chem. Intermed. 22, 255 (1996); Y. Chen, T. Urano, T. Karatsu, S. Takahara, T. Yamaoka, and K. Tokumaru: J. Chem. Soc., Perkin Trans. 2, 1998, 2233.