Modern trends in physical organic chemistry

Oleg M. Nefedov and Mikhail P. Egorov

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Prosp., 117913 Moscow, Russia

Biography: Professor Oleg M. Nefedov was born in 1931 in Dmitrov (Moscow region). He graduated from the D. I. Mendeleev Institute of Chemical Technology in 1954, and received the Ph.D. degree in 1957 and the Doctor of Sciences degree in 1967, both at the Institute of Organic Chemistry of the USSR Academy of Sciences. Since 1968 he is the head of the Laboratory of Carbene and Small Ring Chemistry. In 1987 he was elected as a full member (Academician) of the USSR Academy of Sciences—Russian Academy of Sciences, and since 1988 he is the Vice-President of the USSR Academy of Sciences—Russian Academy of Sciences. He is a pioneer in the chemistry of short-lived reactive intermediates with low-coordinated carbon, silicon and germanium atoms. He was awarded the USSR State Prize, (twice), the N. D. Zelinsky Prize (Moscow, USSR), the special Award of the USSR and Hungarian Academies of Sciences, the N. N. Semenov Prize (Moscow, USSR), and the A . P. Karpinsky Prize (Hamburg, BRD).

Dr. Mikhail P. Egorov was born in 1953 in Zvenigorod (Moscow region). He graduated from the Department of Chemistry of M. V. Lomonosov Moscow State University (MSU) in 1976, and received his Ph.D. degree in 1980 at MSU and his Doctor of Sciences degree in 1992 at the Institute of Organic Chemistry of the USSR Academy of Sciences. Since 1984 he has been working at the Laboratory of Carbene and Small Ring Chemistry headed by Professor Nefedov; he is research group head. His research interests lie in the field of physical organic and organometallic chemistry.

Physical organic chemistry is one of the rapidly developing branches of chemistry and the question of what it will looks like in the 21st century is of great interest. In this short essay we attempt to summarize our view on the main trends in the development of this area of chemistry.

In the preface to the second edition (1970) of the classical monograph *Physical Organic Chemistry* Louis Hammett defined this area of chemistry as an interdisciplinary science which main purpose is the investigation of organic chemistry phenomena by quantitative mathematical methods (1). It mostly included the studies of mechanisms of chemical reactions by quantitative methods and the effects of the structure of the reagents and the nature of the medium on the reactivity.

Physical organic chemistry has changed significantly since that time. It moved from empirical regularities toward understanding the very fine effects of electronic structure and of intra- and intermolecular interactions on the reactivity and reaction mechanisms of the substrates. Three main factors played an important role in this process. The first one is the development and wide application of sophisticated experimental physical chemical and theoretical quantum chemical methods to study the electronic structure, geometry, and thermodynamic and kinetic parameters of molecules, especially of short-lived reactive intermediates. Many of these experimental methods, *e.g.*, low temperature matrix isolation, laser flash photolysis, and other time resolved techniques allow one to observe these species directly. The appearance of new powerful physical chemical methods such as, *e.g.*, femtosecond laser flash photolysis, the use of noble gas cryosolutions, recent achievements in spin chemistry and magnetic field effects, and new procedures in mass spectrometry and NMR spectroscopy open wide possibilities to study reactivity and reaction mechanisms at a much higher conceptual level.

The second factor is related to the objects which are studied now by physical organic chemistry. They include not only organic substrates. For example, it is hard to overestimate the role of organometallic compounds, macromolecules, and natural materials in modern organic chemistry. As a result of the tight integration of organic chemistry with the neighboring areas of chemistry the systems studied by physical organic

chemistry often include such objects. This can be clearly seen if one looks through the proceedings of recent conferences on physical organic chemistry. The third factor that is related to the second one is the increasing influence of ideas and concepts from other areas of chemistry, *e.g.*, bioorganic and organometallic chemistry, photochemistry, computational chemistry, *etc.*

A characteristic tendency of the development of modern physical organic chemistry is the use of a complex approach in which two or more different techniques are applied to the system under study. Such a multi-technique approach provides the opportunity to obtain a comprehensive picture of the phenomenon studied and to increase considerably the reliability of the results obtained and their interpretations. Combination of various experimental methods or experimental and theoretical methods is possible. The latter are becoming more attractive due to the huge progress in computer technology, the availability of personal computers, and the rapid development of user-friendly programs which enable the experimental chemist to carry out semi-empirical or *ab initio* calculations of a sufficiently high level (*e.g.*, HyperChem, GAUSSIAN for Windows, *etc.*). Rapid development of quantum chemical approaches and models allowing one to take into account the effects of solvation makes the results of calculation closer to the those obtained in a real "flask" by experimental chemists.

Analysis and prediction of reactivity of organic substances, the problems of structure activity(property) relationships, and computer assisted reaction design have become the subjects of growing interest among chemists. As the accuracy of these methods increase they will attract organic chemists more and more.

Physical organic chemists pay increasing attention to the reactive intermediates of chemical reactions. Reactivity of these species in fact determines the reaction pathways. Three main approaches had been applied to study reactive intermediates: (i) the use of time-resolved techniques for the study of short-lived species; (ii) stabilization of reactive intermediates in low temperature matrices and their detection by different spectral methods (UV, IR, Raman, ESR spectroscopy, *etc.*); (iii) kinetic and thermodynamic stabilization of short-lived species using electronic and steric effects of the substituents. The later approach is very attractive to organic or organometallic chemists but has one serious disadvantage: the electronic structure and geometry of such "stable reactive intermediates" may be severely distorted compared to those of short-lived ones.

Many chemical reactions considered by physical organic chemistry suggested the participation of reactive intermediates of one particular type (*e.g.*, ions, radicals, radical ions, carbenes). In fact, nature turns out to be more complicated and in many cases the reaction pathways were found to include the transformations of one reactive intermediate into another one. Direct detection of each intermediate arising in the course of the reaction and study of their reactivity is of great importance. We will give some examples of such reactions from the chemistry of carbene analogs, which is a subject of particular interest of the authors.

Searching for good precursors of silylenes, germylenes, and stannylenes is one of the urgent problems of the chemistry of carbene analogs. Currently the derivatives of 7-heteronorbornadienes are considered to be convenient sources of these species upon thermolysis or photolysis. Two mechanisms were discussed for generation of carbene analogs from these sources: concerted and non-concerted. The latter includes the formation of short-lived biradical or zwitterionic species as the precursors of silylenes (germylenes). Using 1H CIDNP and flash photolysis techniques the mechanism of photochemical generation of Me_2E (E = Si, Ge) from 7,7-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-sila(germa)norbornadienes has been studied (2-5). The results obtained by both methods were mutually complementary and provided very strong evidence for the existence of 1,5-biradicals formed by homolysis of the endocyclic Si(Ge)-C bond in 7-heteronorbornadienes. These short-lived biradicals were in fact the precursors of other reactive intermediates - the silylenes and germylenes, which have been also detected by flash photolysis technique (2, 5).

Many insertion reactions of carbene analogs into R-X bonds were considered to occur as radical processes. Typically, an atom transfer mechanism including a halogen atom abstraction by a carbene analog was considered for these reactions (2, 6, 7). However, the detailed study of the mechanism of the reaction has shown that an electron transfer can be the first key step in this transformation (8). The proposed mechanism includes the formation of the carbene analog radical ions, a poorly understood class of reactive intermediates. Later the direct evidence for the existence of such hypervalent radical ions was obtained by the ESR technique (9) and by cyclic voltammetry (10). Lifetimes and the ways of decomposition of the carbene analog and a substrate radical ion determine the reaction products.

It should be pointed out that, in general, the elucidation of the role of electron transfer in organic and

organometallic reactions still remains one of the fundamental problem of physical organic chemistry. Therefore, interest in charged reactive intermediates, in particular radical ions of different species, increases rapidly. Low temperature matrix isolation and laser flash photolysis are used with increasing frequency, along with traditional methods (ESR spectroscopy, CIDNP technique, mass spectrometry, electrochemistry) to study these species.

A new stage in studies of complexation is currently being observed. This process is commonly accepted as the first and sometimes the key step of many chemical reactions. Complexation is found to be a powerful means of changing the reactivity of organic and organometallic species. Previously the information about complex formation was mainly based on kinetic studies and electronic absorption spectra. Very few data concerning electronic structure, geometry, and reactivity of such complexes were available. More and more publications dealing with the comprehensive investigations of complexation between molecules of different types are appearing in chemical journals. In these studies the modern sophisticated experimental and quantum-chemical methods are widely used. For example, low temperature matrix isolation, laser flash photolysis, the CIDNP technique, and quantum chemical calculations were used recently in different combinations to study in details the complexation of silylenes, germylenes, and stannylenes with different agents: Lewis bases, alkenes, alkynes, aromatics, alkyl halides, and even dinitrogen (2, 5, 11-13). As a result many short-lived complexes were detected, and their spectral properties, electronic structure, geometry and reactivity were studied. In some cases complexation with a Lewis base results not only in the change of rate constants, but it can change the pathways and the mechanisms of the reactions of germylenes and silylenes (2). One may expect that complexation will continue to receive the growing attention of chemists in the near future.

REFERENCES

1. L. P. Hammett, *Physical Organic Chemistry. Reaction Rates, Equilibria and Mechanisms*. McGraw-Hill, New York (1970).
2. O. M. Nefedov and M. P. Egorov, in *Frontiers of Organosilicon Chemistry*, A. R. Bassindale and P. P. Gaspar Eds., Royal Society of Chemistry, 145 (1991).
3. S. P. Kolesnikov, M. P. Egorov, A. M. Galminas, M. B. Ezhova, O. M. Nefedov, T. V. Leshina, M. B.Taraban, A. I. Kruppa and V. I. Maryasova. *J. Organomet. Chem.* **391**, C1 (1990).
4. M. P. Egorov, M. B. Ezhova, S. P. Kolesnikov, O. M. Nefedov, M. B. Taraban, A. I. Kruppa and T. V. Leshina. *Mendeleev Commun.* 143 (1991).
5. M. B. Taraban, V. F. Plyusnin, O. S. Volkova, V. P. Grivin, T. V. Leshina, V. Ya. Lee, V. I. Faustov, M. P. Egorov and O. M. Nefedov. *J. Phys. Chem.* **99**, 1479 (1995).
6. P. P. Gaspar, in *Reactive Intermediates*, M. Jones and R. A. Moss, Eds, John Wiley & Sons, Vol. 1 (1978);Vol. 2, (1981); Vol. 3 (1985).
7. W. P. Neumann. *Chem. Rev.* **91**, 311 (1991).
8. M. P. Egorov and O. M. Nefedov. *Main Group Metal Chem.* **19**, 367 (1996).
9. M. P. Egorov, O. M. Nefedov, T.-S. Lin, and P. P. Gaspar. *Organometallics*. **14**, 1539 (1995).
10. V. Ya. Lee, A. A. Basova, I. A. Matchkarovskaya, V. I. Faustov, M. P. Egorov, O. M. Nefedov, R. D. Rakhimov and K. P. Butin. *J. Organomet. Chem.* **499**, 27 (1995).
11. S. E. Boganov, V. I. Faustov, M. P. Egorov and O. M. Nefedov. *Russ. Chem. Bull.* **43**, 47 (1994).
12. S. E. Boganov, V. I. Faustov, M. P. Egorov and O. M. Nefedov. *High Temp. Sci.* **33**, 107 (1995).
13. S. E. Boganov, V. I. Faustov, M. P. Egorov and O. M. Nefedov. Russ. *Chem. Bull.* **45**, 1121 (1996).