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OBITUARY

PROFESSOR O. Yu. OKHLOBYSTIN

Ya. Stradyn'

Oleg Yur'evich Okhlobystin died suddenly in Astrakhan on February 22 1994. He was a notable Russian chemist, a man with a daring mind, sincere generosity, with great talent and overflowing with ideas. He was widely known for his work in organometallic chemistry and Professor O. Yu. Okhlobystin's work on one-electron transfer played an activating role in the field of heterocyclic chemistry.

O. Yu. Okhlobystin was born in Moscow in 1932 and entered the Chemistry Faculty of the M. V. Lomonosov Moscow University in 1954 where he later defended his candidate's thesis (Synthesis of Organometallic Compounds Using Aluminium Alkyls, 1961). His doctoral thesis (The Role of Specific Solvation and Complex Formation in Organometallic Reactions) was defended in 1971 at Rostov University (Rostov-on-Don) to which O. Yu. Okhlobystin transferred after 17 years of work in the Institute of Elementoorganic Compounds, USSR Academy of Sciences, Moscow. O. Yu. Okhlobystin was deputy science director of the Science Research Institute for Physical Organic Chemistry, Rostov State University from 1971 to 1981. From 1981 to 1992 he held the chair of organic and physical chemistry at Severo-Osetinsk (North Osetia) State University in Vladikavkaz (Ordzhonikidze). In September 1992 he moved from Vladikazkaz to Astrakhan where he held the chair of organic, biological, physical, and colloid chemistry in the Astrakhan Technological Institute for the Fishing and Agricultural Industries. With his wife, doctor of chemistry N. T. Berberova, he attempted to set up conditions for scientific work and succeeded well: he set up the equipment necessary for electrochemical measurements, he acquired spectrometric and chromatographic apparatus, he was wholeheartedly determined to continue the beginnings made at Vladikavkaz and had planned new investigations. However this was not to be .... It is hoped that the research begun in Astrakhan will be developed under the leadership of Professor N. T. Berberova.

O. Yu. Okhlobystin authored about 450 scientific publications, including 44 patents and 15 books. He supervised 25 candidates and 8 doctoral dissertations ; he was a member of the Scientific Committees on Electrochemistry and Elementoorganic Chemistry of the Russian Academy of Sciences. Unfortunately, he failed by three votes to be elected Corresponding Member of the Russian Academy of Sciences at one of the recent elections; it is pertinent to quote here the citation of O. Yu. Okhlobystin's basic scientific achievements put forward in support of his election:

"At the beginning of his scientific work at the Institute of Elementoorganic Chemistry, USSR Academy of Science, O. Yu. Okhlobystin (along with L. I. Zakharkin and V. V. Gavrilenko) was the first scientist in the USSR to carry out the "direct" Ziegler synthesis of organoaluminum compounds, as a result of which successful methods were developed for the synthesis of a variety of elementoorganic compounds based on alkylaluminum compounds. He was the first to demonstrate the general nature of alkyl group exchange in compounds of boron, zinc, aluminum and beryllium; he was the first to observe "anti-thermodynamic" isomerisation of secondary alkyl groups to primary in the case of trisisopropylaluminum.

Later he was the first to prepare stable aromatic boron clusters, the carboranes and to carry out the basic investigation of their properties (with L. I. Zakharkin, V. I. Stanko, et al.). With V. I. Bregadze he was the first to carry out a systematic study of the C-substituted carboranes and to observe a series of their unusual properties.

At the end of the 1960s O. Yu. Okhlobystin developed a simple and successful method for the preparation of unsolvated organomagnesium compounds in the absence of ether or any other Grignard reaction catalyst. This observation led to the development of a number of successful industrial methods for the preparation of elementoorganic compounds, in particular organotin compounds and some otherwise difficult to obtain organophosphorus derivatives (with B. N. Strunina). At the same time the powerful catalytic effect of such strongly solvating ethers as dimethoxyethane on exchange reactions involving organomagnesium compounds was observed (with K. A. Bilevich and L. I. Zakharkin) and it was shown that the phenomenon was a general one: in the absence of complicating factors complex formation sharply increased the nucleophilicity of organo-

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metallic compounds in exchange reactions. Before this work a different view of organometallic chemistry predominated. The degree of solvation of organomagnesium compounds determines the character of subsequent reactions. In strongly solvating media the formally heterolytic Wurtz reaction predominates while exchange in hydrocarbon media occurs completely by a free radical pathway.

O. Yu. Okhlobystin's studies on intramolecular coordination in functionally substituted organometallic compounds revealed some unexpected rearrangements of nitromethyl derivatives of mercury in organomercury fulminates and he was the first to obtain stereochemically pure *cis*-β-chlorovinyl derivatives of mercury which had been assumed for many years to be a mixture of the *cis*- and *trans*-isomers (with A. N. Nesmeyanov and A. E. Borisov).

Towards the end of the 1960s O. Yu. Okhlobystin suggested that many formally heterolytic reactions in fact included a redox stage in which free ion radicals and free radicals were formed as intermediates. The correctness of this suggestion was demonstrated subsequently by O. Yu. Okhlobystin himself and many others for a large and varied number of examples. In particular the treatment of direct metallation of C-H acids as a simple acid-base process was shown to be incorrect (A. I. Shatenshtein). In fact reactions of this type begin with reduction of the substrate to the corresponding anion radical and only subsequent reaction of the latter gives rise to the carbanion. Dehydrogenation of many compounds, which was previously treated as a one step loss of a hydride ion, in fact goes via initial oxidation of the substrate to a cation radical with subsequent deprotonation and secondary oxidation. Current electrochemical methods, kinetics and EPR spectroscopy were widely used in these studies. Cation radicals and free radicals of many heterocyclic compounds and elementoorganic hydrides were obtained for the first time and their properties were studied. Effective methods for the electrochemical initiation of the hydrometallation of olefins (in particular hydrosilylation) in the absence of the normal catalysts were developed as a result of these observations. On the other hand the known stepwise dehydrogenation of biological substrates of the NAD-H type revealed the catalytic role of riboflavin (vitamin B_2) in dehydrogenation reactions with molecular oxygen and lead to the proposal of more effective catalysts for similar reactions (with N. T. Berberova). Many "normal" dehydrogenation reactions (conversion of hydrazobenzene to azobenzene, 4H-pyrans into pyryllium salts, leucobases into the cation form of dyes) were shown to be vigorously catalysed by traces of oxygen. Oxygen was also shown to sensitise compositions for photothermal recording of information.

With A. S. Morkovnik he obtained valuable insight into the redox nature of electrophilic aromatic substitution during formation of the π-complex. It was shown that in a large number of cases the reaction began by oxidation of the substrate to the cation radical which was only later converted to the σ-complex.

In recent years O. Yu. Okhlobystin began a systematic study of the very broad class of complexes and organometallic compounds containing redox ligands. Oxidation (reduction) of such compounds gives rise to free valency in the ligand without a concomitant change in the valence state of the metal. Functional derivatives of sterically hindered phenols, 4H-pyrans and pyryllium salts, viologens and phenoxazines are commonly used redox ligands, while main group and transition metals and organometallic units up to and including uranium were used as the complexed metals. Useful methods for the study of the influence of complex formation on the stability of free radicals and ion radicals were discovered. In some instances the effects were very large. For example, introduction of platinum into the aromatic structure of a screened phenoxyl led to a free radical with phenomenal stability to heat and oxygen. The presence of an unpaired electron on the ligand allows the successful investigation of the structures of complexes and organometallic compounds by EPR spectroscopy. In a number of cases the creation of free valency on the ligand lead to rapid structural change, e.g., rapid *meta*- to *ortho*-rearrangements in carboranes, C-bonded to pyranyl free radicals, and reverse Beckman rearrangements in the cation radical of 2,4-di-*tert*-butylacetophenone oxime. Clearly O. Yu. Okhlobystin and his co-workers observed the phenomenon of intramolecular electron transfer from the metal to the cationic ligand leading to the reversible formation of free valences in the ligand ("electron tautomerism"). Among the complexes with free radical ligands were effective low temperature catalysts for the vulcanisation of vinylsiloxane rubbers which allowed for the production of ultrahigh frequency composites for the electronics industry which exceeded the world's best examples in electrophysical characteristics (implantation processing)".

This presentation on Professor O. Yu. Okhlobystin would not be complete without reference to his work on the history of chemistry and his popular science books: O. Yu. Okhlobystin, Third Course in Chemistry, A. N. Nesmeyanov (ed.), Nauka, Moscow (1965) (translated into Japanese and Spanish); O. Yu. Okhlobystin, Dreadful Chemistry, Rostov State University Press, Rostov-on-Don (1980), 2nd ed. Nauka, Moscow (1989); O. Yu. Okhlobystin, The Life and Death of Chemical Ideas, Nauka, Moscow (1990). He published a number of reviews on the history of organometallic chemistry and a series of important articles on the problems of higher education in chemistry (in the journal Khimiya i Zhizn' (Chemistry and Life) and the magazines Literaturnaya Gazeta, Komsomol'skaya Pravda, etc.). O. Yu. Okhlobystin's vigorous temperament and broad erudition are very evident in these publications; this is particularly the case in his scientific papers which are rich in original ideas and which always stimulated discussion and did not allow his colleagues to fall asleep.

The memory of O. Yu. Okhlobystin will remain for a long time with all those who knew this extraordinary man.

All those who knew him will not soon forget this extraordinary man, O. Yu. Okhlobystin.