Information

Scientific Centers of the World

Institute of Chemical Kinetics and Combustion of the Siberian Branch of the Russian Academy of Sciences*

In 1940—1950, chemical kinetics became one of the leading branches of chemistry, among other reasons, owing to the achievements of the scientific school of N. N. Semenov. The unremitting interest of scientists in this field of research is due to the fact that understanding of the mechanisms of chemical reactions and of the laws of their development in time makes it possible to control many chemical processes.

In 1957, Academician N. N. Semenov supported the initiative of Academician M. A. Lavrent'ev to found the Siberian Branch of the Academy of Sciences and suggested that his disciples V. V. Voevodsky and A. A. Koval'sky should organize the Institute of Chemical Kinetics and Combustion in Novosibirsk (ICK&C).

At that time, the scientific interests of A. A. Koval'sky were associated with combustion of solid propellants. A further area of research, the physics and chemistry of aerosols and their application, was developed under his leadership at the ICK&C. A. A. Koval'sky also paid much attention to the investigation of combustion processes in gases.

Corresponding Member of the Academy of Sciences A. A. Koval'sky headed the Institute from 1957 till 1972. Academician V. V. Voevodsky, who was Deputy Director of the Institute until he passed away in 1967, laid the basis for the development of the research on mechanisms and rates of chemical reactions. The scientific lines of the Institute were conclusively formed in the 70—80s under the leadership of its Director (up to 1993) Academician Yu. N. Molin. At present, the following lines of research are being actively developed at the ICK&C:

(1) studies on elementary acts and mechanisms of chemical transformations, in particular, those occurring during photochemical and radiation-induced reactions, by means of modern techniques of theoretical physics;

(2) studies on the mechanisms of combustion in the gas and condensed phases;

(3) studies on the processes of formation and propagation of artificial aerosols and their practical application;

(4) development of new techniques and instruments for studies in physical chemistry;

(5) elaboration of procedures for synthesis of organic compounds with conjugated bonds and investigation of their chemical properties.

More than 300 persons work at the 13 laboratories and 4 research groups of the Institute. They include 164 research workers, 26 of which are Doctors of Sciences and 82 are Ph. D.

Below we present the most important, in our opinion, results obtained at the ICK&C on the two first lines of research over the last 10 years.

Perhaps, the theoretical and experimental development of the problem of elementary acts, taking into account the spin state of a system consisting of a pair of neutral radicals, radical ions, or charges, may be considered to be the most significant achievement. This

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line of research, spin chemistry, appeared at the Institute as early as 1972. In recent years, vibrational and resonance effects were discovered in the kinetics of recombination of radical-ion pairs, these effects being caused by the coherence of the initial spin state of the pair and by the evolution of the coherence during a chemical reaction. The effects were found to depend on the intensity of an external magnetic field. The resonances observed in the case of low magnetic fields can be a real physical mechanism by which low magnetic fields affect biological objects.

The methods of spin chemistry are used to study kinetics and mechanisms of reactions in the chemistry of organometallic compounds. For example, study of the chemically induced dynamic nuclear polarization has made it possible to determine the multiplicity of reacting states and to establish the structure of main paramagnetic precursors of the products of photolysis of silicon-, germanium-, and tin-containing ketones.

A method of laser pulse photolysis with a time resolution of 50 ns and a sensitivity with respect to optical density of $5 \cdot 10^{-4}$ has been developed. The primary acts in the photochemistry of halide complexes of platinum and iridium were studied. It was shown that, unlike the generally accepted views, the primary processes in this case are reactions of electron transfer from solvent molecules to the excited complex, and the radical complexes that dissociate to give free radicals over periods of nanoseconds are the primary species.

The method of laser pulse photoinjection of electrons from a metal into water or aqueous solutions was used to determine the lengths of electron thermalization depending on their energy (up to 5 eV), to identify the radicals of various halogen-substituted benzoic acid derivatives from time-resolved (up to 10^{-9} s) polarograms, and to determine their lifetimes and thermodynamic characteristics.

Using selective laser photochemistry, the possibility has been shown of conducting thermal gas-phase reactions under purely homogeneous conditions (*i.e.*, without participation of reactor walls) under the action of radiation of a continuous CO_2 laser. Besides, the kinetics of these reactions was studied.

"Noncollisional" IR multiphoton dissociation of molecules under radiation of a pulsed CO_2 laser and the reactivities of vibrationally excited molecules and radicals have been studied. Methods for the separation of isotopes using the selective IR multiphoton dissociation were developed.

In recent years, much attention has been paid to the development of novel radiospectroscopic methods and their application to kinetics. New ESR techniques were proposed, namely, the method of pulsed electron-electron double resonance, the ESR tomography with the detection by the electron spin echo signal, the method of optically detected ESR, the method of electron-nuclear resonance of radical pairs, and the kinetic modification of the method of laser magnetic resonance. A technique of stimulated nuclear polarization was developed to study the magnetic-resonance characteristics of short-lived radical pairs in liquid-phase reactions.

The groundwork has been laid for the high-resolution ESR spectroscopy based on the Fourier analysis of modulation phenomena in the electron spin echo (ESEEM). This method has found wide use in the studies of the nearest environment of various paramagnetic centers (trapped electron, atoms, radicals, catalytic and photochemical systems, and spin labels in biological systems). Based on the electron spin echo, methods for determining the molecular mobility of spin labels and probes in the range of slow and superslow motions (10^3—10^7 Hz) were developed.

Theory of the use of all the novel radiospectroscopic methods in chemistry has been developed. This theory makes it possible to obtain unique structural or kinetic information from experimental data and from analysis of new effects. Thus the optically detected ESR has made it possible to detect with a record-breaking sensitivity the primary radical pairs in radiation-induced and photochemical processes with lifetimes of up to 10^{-9} s.

The pulse ESR methods have allowed information on the spatial characteristics of elementary acts to be obtained for the first time. In particular, the method of electron spin echo was used to show that the radicals formed upon irradiation are stabilized in polar matrices at low temperatures in radical tracks, whose spatial structure is determined by the path lengths of secondary electrons and by the distances by which positive charge migrates. The radical-ion pairs arising on the photolysis of matrices containing transition metal ions were studied. The changes in the function of paired space distribution of radical and atoms in these matrices during diffusion and chemical reactions were investigated.

In recent years, a new scientific branch, filtrational gas combustion, has been developed at the ICK&C. This is a new class of filtrational combustion processes, which is characterized by a gas-phase chemical reaction running in an inert porous medium. Previously unknown stationary frontal combustion processes were found, namely, slow and fast waves of filtrational combustion, hybrid waves, waves with filtrational combustion of a liquid, and waves with vaporization-diffusion mechanism of propagation. Physical and mathematical models for these processes were developed. The fundamental studies of filtrational combustion of gases provided the basis for the development of principally novel heat generators and energy-saving technologies Based on these studies, some nontraditional solutions of the problems of fire and explosion safety were found.

The method of probing mass spectrometry with soft ionization by electron impact and modeling of elementary stages were used to study the structure of the $H_2/O_2/Ar$ flames, including those with organophosphorus compounds added, which are models of the chemical warfare agent Sarin. A mechanism, that accounts for the characteristic features found, was proposed. These results

are significant for the justification of the ecological safety of technologies for the destruction of chemical weapons.

Studies dealing with the visualization of the process of combustion of highly energetic solids are being intensely carried out at the Institute. The formation of a porous reaction layer and its dispersion are important features of the combustion of substances in a liquid layer on a burning surface. Using holography and rapid filming with highly intense pulse lighting, the degree of mechanical destruction of the reacting layer was measured for the first time and the regularities of this process were established. Optical methods also provided valuable information on the formation of agglomerates during combustion of propellants or compositions containing metallic particles. These data are highly significant for estimating the efficiency of the use of a metallic component in the combustion of propellants and for calculating the energy losses during the operation of rocket engines.

The Institute maintains and broadens its international relations on all the main lines of research and holds international schools, seminars, and conferences. For example, joint studies carried out by researchers of ICK&C together with scientists of 40 foreign universities, scientific centers, and institutes have been reported over the last 5 years. In 1993—1996, workers of the Institute received 24 grants from the International Foundations INTAS, ISF, NATO, *etc.* Within the framework of the international cooperation programs, systematic studies on the following subjects are being carried out: "Conversion of light energy into chemical energy during photosynthesis" (Japan, Netherlands), "Aerosols of Siberia" (Belgium, Germany), "Spin chemistry" (Germany, Japan, Switzerland, UK, USA), "Combustion of solid propellants" (Italy, Netherlands, USA), "Development of the instrumentation for chemical radiospectroscopy" (Germany, Netherlands, USA).

The 40-year experience of the ICK&C has shown that the prospects of further development of all the lines of research of the Institute are closely connected to the elaboration and application of modern experimental techniques in the field of chemical physics. At presents, there are two ways, *i.e.*, the development of these techniques at the ICK&C and research work carried out at well equipped foreign laboratories according to joint projects. For example, the ICK&C together with the Institute of Nuclear Physics of the Siberian Branch of the RAS have developed a program aimed at the foundation of the Photochemistry Center of the Siberian Branch of the RAS. Based on the free-electron laser, studies on the selective laser photochemistry have been started. Further development of a conventional research line of the Institute, chemical radiospectroscopy, including, first of all, elaboration of new radiospectrometric methods is also planned. We hope that this will be possible at the Center of Chemical Radiospectroscopy of the Siberian Branch of the RAS, which was organized recently at the Institute with financial support from the Russian and foreign scientific organizations and foundations.

Thus, elaboration and improvement of the experimental base, wide international cooperation, and leaning on the inter-institute relations within the Novosibirsk Scientific Center of the Siberian Branch of the RAS comprise the basis for the future development of the scientific research at the ICK&C.

Congresses, Conferences, Symposia, Meetings, and Seminars in the Field of Chemical Sciences Held in 1996—1997

II Baku International Petrochemical Conference "Petrochemistry of XXI Century: New Processes, Technologies, and Materials" Dedicated to the Memory of Academician Yu. G. Mamedaliev

Baku, Azerbaidzhan (Institute of Petrochemical Processes of the Azerbaidzhan Academy of Sciences, 30 ul. Tel'nova, 370025 Baku, Azerbaidzhan).
June 18—21, 1996.

XIII International Conference on Chemical Reactors (KHIMREAKTOR-13)

Novosibirsk, Russian Federation (G. V. Zamulina, G. K. Boreskov Institute of Catalysis of the Siberian Branch of the RAS, 5 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation. Tel.: +7 (383 2) 350 237. Fax: +7 (383 2) 355 766. E-mail: staza@catalysis.nsk.su).
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