MEETINGS AND CONFERENCES

Scientific Session of the Division of General Physics and Astronomy and the Division of Nuclear Physics of the Academy of Sciences of the USSR [25–26 June (1986)]

A Joint Scientific Session of the Division of General Physics and Astronomy and the Division of Nuclear Physics of the Academy of Sciences of the USSR was held on June 25 and 26, 1986, at the S. I. Vavilov Institute of Physics Problems of the Academy of Sciences of the USSR. The following reports were presented at the session.

June 25

1. *A. L. Buchachenko, Yu. N. Molin, R. Z. Sagdeev, K. M. Salikhov, and E. L. Frankevich.* Magneto-spin effects in chemical reactions.

2. *I. M. Barkalov and V. I. Gol'danskiĭ.* Autowave propagation of cryochemical reactions in a solid phase.

3. *V. B. Braginskiĭ and L. P. Grishchuk.* Gravitational wave astronomy.

4. *N. S. Kardashev, V. N. Lukash, and I. D. Novikov,* Observational cosmology and cosmological models.

Summaries of the presentations are given below.

A. L. Buchachenko, Yu. N. Molin, R. Z. Sagdeev, K. M. Salikhov, and E. L. Frankevich. *Magneto-spin effects in chemical reactions.* Many elementary physico-chemical processes proceed with the participation of pairs of paramagnetic particles. Examples of such processes are the triplet-triplet annihilation of excitons in molecular crystals, the recombination of electrons and holes in semiconductors, the separation of charges during the primary stage of photosynthesis. Here belongs also a wide class of chemical reactions of the breaking up of molecules with the formation of free radicals and recombination of radicals. The reactive ability of particles in these processes depends on the multiplet nature of the electronic state of the pair of reagents. Interaction of electrons with external constant and variable magnetic fields, hyperfine interaction with nuclei, processes of paramagnetic relaxation, etc., change the multiplet nature of pairs of reagents and as a result influence the yield of a reaction.

The spin dynamics in pairs of reagents under the influence of magnetic interactions leads to a number of remarkable consequences. In the products of radical reactions one can observe a nonequilibrium population of nuclear spin states—the phenomenon of chemical polarization of nuclei (CPN), and stimulated polarization of nuclei (SPN). In the CPN processes a preferential orientation of nuclear spins relative to the external magnetic field and a mutual ordering of nuclear spins are produced in the course of the reaction. In the SPN processes an increase or decrease in the population of very definite configurations of nuclear spins occurs under the influence of radio-frequency pumping. Simultaneously polarization of electron spins occurs. The polarization of spins in radical reactions finds application, for example, in establishing the detailed mechanism of the reactions, in recording EPR spectra of short-lived intermediate states such as radical pairs, etc.

Due to the fact that the rate of change of the multiplet nature of pairs of paramagnetic reagents depends on the strength of an external magnetic field, one can observe a magnetic effect in the physico-chemical processes under discussion: the yield of products and the reaction rates change with increasing magnetic field strength. The effects of a magnetic field have been established in the photoconductivity of molecular crystals, in the liquid-phase radical reactions, in the recombination of electrons and holes in semiconductors, in the charge separation in the first stage of the photosynthesis process, in recombinative luminescence during radiolysis, etc.

The magnetic effects provide unique information about the spin, molecular, and chemical dynamics of intermediate states, i.e., pairs of paramagnetic reagents. A convincing demonstration of the spin dynamics of radical pairs is the observation of oscillations in recombinative luminescence. The influence of variable magnetic fields on the yield of reaction products has a resonant character, and this allows one to develop new, exceptionally sensitive methods for detection of magnetic resonance spectra of short-lived pairs of paramagnetic particles. An important and interesting demonstration of the spin dynamics of radical pairs is the magnetic isotope effect. The efficiency of the singlet-triplet transitions in radical pairs depends on the hyperfine interaction and changes, therefore, with isotope substitution. The magnetic isotope effect has been observed in hydrogen (H and D), carbon (^{12}C and ^{13}C), nitrogen (^{14}N and ^{15}N), oxygen (^{16}O, ^{17}O and ^{18}O). Research on heavy elements is underway. The magnetic isotope effect signifies the existence of a new principle for fractionation of isotopes in nature.

The aforementioned magnetic and spin effects in elementary physico-chemical processes demonstrate the role of quantum selection rules in these reactions and the possibility of controlling these reactions with the help of magnetic interactions. The results obtained in this area have significantly changed our concepts about the role of relative weak magnetic interactions in chemical reactions.

[1]I. A. Sokolik and E. L. Frankevich, Usp. Fiz. Nauk **111**, 261 (1973) [Sov. Phys. Uspekhi **16**, 687 (1973)].

[2]A. L. Buchachenko, R. Z. Sagdeev, and K. M. Salikhov, Magnetic and spin effects in chemical reactions (In Russian), Ed. by Yu. N. Molin,

Nauka, Novosibirsk, 1978.

[3]K. M. Salikhov, Yu. N. Molin, R. Z. Sagdeev, and A. L. Buchachenko, *Spin Polarization and Magnetic Effects in Radical reactions*, Ed. Yu. N. Molin, Elsevier, Amsterdam; Akadémiai Kiadó, Budapest, 1984.

I.M. Barkalov and V. I. Gol'danskiĭ. *Autowave propagation of cryochemical reactions in a solid phase.* Only recently the very possibility of a chemical reaction proceeding spontaneously (i.e., of a transformation accompanied by a change of the length and angle of interatomic bonds with a corresponding re-grouping of atoms) in the solid state in the vicinity of the absolute zero was in doubt. The attitude has changed after the discovery of the phenomenon of low-temperature limit of the rate of chemical reactions, an example of which is the growth of chains during polymerization of formaldehyde.[1] As is well known, the concept of tunneling transitions in chemical kinetics has received a wide development in later works.[2]

In this presentation we consider another class of cryochemical solid phase reactions—those taking place as a result of the transformation of mechanical energy into chemical energy and developing due to the positive feedback between brittle destruction of the solid and a chemical reaction in the surface (and the near-surface) layers of fresh cracks. This feedback is due to the fact that the chemical reaction leads to further brittle destruction of the sample caused by the density or temperature gradients due to it, which give rise the stresses destroying the sample. The systems with a feedback described by an appropriate nonlinear model have characteristic autowave phenomena arising in a sample of sufficient extension in response to a local perturbation.

For all the systems that have been studied (chain reactions of chlorination, hydrobromination of olefins and polymerization in glasslike and polycrystalline samples), which are chemically inert at 4.2 and 77 K, it was possible, using local brittle destruction, to initiate spontaneous propagation of a reaction wave. This wave could be easily recorded wi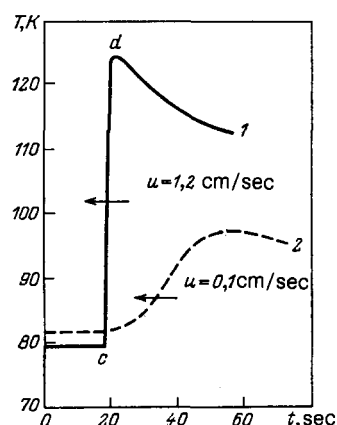th the aid of cinematography. The reaction wave was propagating along a sample with the speed 10–12 mm/sec, changing little when the thermostat temperature varied from 77 to 4.2 K. A typical profile of the propagating temperature wave (Fig. 1, curve 1) has some characteristics very unusual for the classical thermal self-propagation, i.e., the absence of an inert heating stage, and abrupt beginning and termination of the reaction in the c and d points.

In order to establish the role of the thermal factor in the mechanism of the phenomena being studied, we tried to find out whether there exists a critical diameter of the sample. When experiments with tubes of 8 mm diameter were changed to experiments with 0.5–1.0 mm diameter capillaries (an increase by more than order of magnitude of the parameter characterizing the intensity of thermal exchange) none of the systems being studied had shown the suppression of the autowave process (Fig. 2). The transition to film samples of 100 mm thickness, directly immersed into liquid nitrogen, also did not lead to the disappearance of the autowave process.

The qualitative picture of propagation of a reaction front in the form of an autowave looks like a displacement along the solid sample of a narrow zone densely covered by an extensive net of newly formed cracks. As was said above, the chemical reaction originates in this zone during the process of brittle destruction and, in turn, creates the conditions for the activating destruction of a neighboring layer. Such layer by layer dispersion is caused by the propagating stress field, which can be caused by 1) the density difference between the initial and final products (appearance of density gradients) and 2) the formation of large temperature gradi-

FIG. 1. Temperature profiles of the autowave propagation of the reaction $C_4H_9Cl + Cl_2$. 1—Initiation of a wave by a local disruption; 2—initiation of a wave by slow local heating.
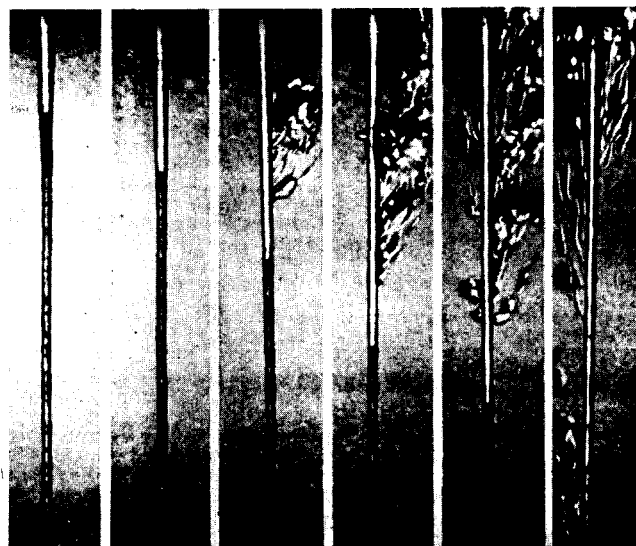

FIG. 2. Cinegram of propagation of an autowave of the chlorination reaction in a capillary with a diameter of 0.5–1.0 mm, immersed in liquid helium.

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