60] Fullerene Fluorination by Molecular Florine in Chemically Active Matrices - A. Kepman, N. Chilingarov, S. Abramov, A. Borshchevsky, I. Golyshevsky, J. Rau, and L. Sidorov (Moscow State University)

A unique feature of a fullerene molecule having 30 double bonds is its ability to form a great variety of derivatives, among which fluorofullerenes are of particular interest. The compositions of fluorofullerenes cover the range from $C_{60}F_2$ to $C_{60}F_{60}$. Introducing of fluorine atoms changes the physical and chemical properties of the fullerene molecule thus explaining growing interest in fluorofullerenes as new promising compounds for material science.

Individual fluorofullerenes ($C_{60}F_{36}$ and $C_{60}F_{18}$) were selectively synthesized by solid-phase reactions of C_{60} with solid fluorinating agents (MnF_3 and K_2PtF_6 respectively) followed by sublimation of volatile products. Utilization of other transition metal fluorides as fluorinating agents does not lead to satisfactory results in the selective syntheses. Direct fluorination of C_{60} by molecular fluorine at 1 atm and more being accompanied by the partial degradation of fullerene cage brought to the selective formation of $C_{60}F_{48}$. These investigations became the starting point of our extensive studies of direct fluorination of fullerene by molecular fluorine in chemically active matrices. In our system we can independently vary the temperature of fluorination, fluorine concentration in the reaction zone (fluorine flow) and the energy of interaction between fluorine and the matrix surface (matrix variation). Thus, we expand the field of searching for the conditions resulting in selective production of various fluorofullerenes. The goal of our work was to elucidate the mechanism of the process, to find the conditions affecting the extent of C_{60} fluorination and as a result to discover the routes for the syntheses of new specific fluorofullerenes.

The Knudsen cell mass spectrometry method with molecular fluorine inlet was employed in our studies. This technique allows one to monitor and to control the fluorination process in the temperature range 500-800 K and molecular fluorine pressure $10^{-4} – 10^{-8}$ atm. A mixture of C_{60} with transition metal fluorides (in high and low oxidation state of the metal) was used to fluorinate by molecular fluorine. Transition metal fluorides were taken in great excess (97% molar excess) over the amount of C_{60} in the initial mixture; therefore, the process can be considered as fluorination of C_{60} by molecular fluorine in matrices of transition metal fluoride. Compositions of the gas phase over the reaction mixture, the partial pressures of fluorination products and the reaction yields were derived from the experimental data.

The first result of our work was that both $C_{60}F_{18}$ and $C_{60}F_{36}$ were selectively obtained in MnF_2 matrix with fluorine inlet at 720 K and 540 K respectively. At the second step of our investigations MnF_3 matrix was used. Under these conditions the gaseous mixture was enriched with highly fluorinated products. Thus, the total content of $C_{60}F_{42}$, $C_{60}F_{44}$, $C_{60}F_{46}$ in mixture was more than 80% at 500 K, while $C_{60}F_{44}$ content being 54%. It should be noted that the fluorination time and the temperature range are of great importance for these processes.

Obtained experimental data were treated using a simple kinetic model, which allows the evaluation of the changes in the concentration of chemically absorbed fluorine and estimation of the differences in activation energies of the following set of reactions: $C_{60}F_{2n}+F_2 \rightarrow C_{60}F_{2n+2}$ (n=17-22).