

Topochemical solid-phase reactions of fluorination
and the problems of selective functionalization
of fullerenes with small inorganic groups

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It is reasonable that the unusual structure of molecules and the original position of fullerenes among organic compounds, marked by combination of the properties of dienes and aromatic compounds, strongly affect the reactivity of fullerenes. Among the peculiarities connected with the specified features the following two ones are of particular interest: (a) great number of reaction sites and (b) small differences in the energies of C-X bonds between atoms C, belonging to the carbon cage, and sequentially attached chemical groups X.

The first one is quite obvious and leads to a great quantity of chemically similar derivatives, varying in number of function groups. As for the second, more or less certain statements are possible only as the new experimental and calculated data is accumulated. This peculiarity presents the main obstacle to synthesis of individual fullerene derivatives – formation of the mixture of different products in the reaction.

The fundamental task for synthesis is conducting a reaction of polyaddition selectively with the highest yield of a product with the desired number of attached atoms. In some cases the problem can be solved relatively easily for the products with maximum number of atoms ($C_{60}F_{48}$, $C_{60}Br_{24}$), when subsequent addition is restricted for pure thermodynamic reasons. However, selective synthesis of the compounds with less number of function groups requires fine compatibility between the rates of addition at different stages of the reaction and the rates of simultaneous removal of the products from the reaction zone. The elimination may occur by various means: through sublimation, evaporation, solution, diffusion or chemical and adsorption binding.

The present work has a summarizing character. In connection with the problem of synthesis of new specific fluoroderivatives of C_{60} the results of study of topochemical reactions of solid-phase fluorination of fullerene with inorganic transition metal fluorides, in which they exhibit variable valence. These reactions occupy a prominent place due to selectivity with respect to such substances as $C_{60}F_{36}^1$ and $C_{60}F_{18}^2$, unachievable with elemental fluorine or other fluorinating agents. They reveal most clearly the peculiarities of fullerenes, already mentioned above, coupled with the very long chain of similar stages of consecutive fluorine addition and the process of eliminations of the products at each stage.

Comprehensive experimental study of the solid-phase fluorination reactions, mainly by mass spectroscopic means, permitted discovering the major regularities in their course, and understand the reason for selectivity. On this basis we have put out a rather simple kinetic model of the reactions, which not only explain the observed behavior, but also possesses considerable predicting power. The agreement between experiment and theory, discovered during its thorough verification, appeared to be much more fine than one could expect keeping in mind the very limited simple presumptions used as the basis for the model.

We think that many features inherent in the solid-phase fluorinating reactions should become apparent in some other reactions of fullerenes – in those characterized by a long sequence of similar stages and elimination of the products from the reaction zone. Therefore the proposed model exceeds the limits of C_{60} fluorination and can be useful in application of reactions of polyaddition in solutions or reactions of fullerenes with gaseous reagents for development of new methods for selective synthesis of fullerene derivatives, including higher fullerenes.

References

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