Topochemical solid-state reactions and problems of selective synthesis of fullerene derivatives

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The characteristic features of polyaddition of small functional groups to fullerenes are considered. The review summarizes the results of experimental and theoretical studies of topochemical solid-state fluorination of fullerene C_{60} with inorganic variable-valence transition metal fluorides and elemental fluorine in chemically active matrices. The thermodynamic and kinetic aspects of the reactions and the factors responsible for selectivity are considered.

Key words: fluorofullerenes, solid-state fluorination, transition metal fluorides, activation energies.

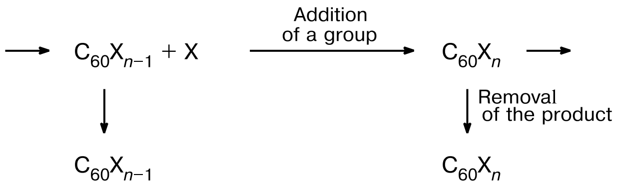
1. Introduction

Selective synthesis of fullerene derivatives is an important field of investigation in organic chemistry. Since fullerenes are spheroidal closed-cage carbon molecules, they exhibit the properties of both polyenes and aromatic compounds. This has a strong effect on the reactivity of fullerenes in polyaddition of functional groups. The characteristic features of these reactions are associated primarily with the facts that, first, fullerenes have a large number of possible binding sites at the double bonds and, second, the C—X chemical bonds between the carbon atoms belonging to the cage and the X groups that are successively bound are similar in energy. A large number of possible binding sites is responsible for the formation of numerous derivatives. The appearance of mixtures of various compounds and isomeric structures in the reaction products resulting from similar C—X bond energies is the major obstacle in the synthesis of individual fullerene derivatives. The present review covers the characteristic features of polyaddition of small functional groups to fullerenes. Particular emphasis is placed on halogen derivatives of fullerene C_{60}.

Halogen derivatives of C_{60} were among the first fullerene derivatives, which have been successfully synthesized. In spite of advances achieved in this field of synthetic chemistry,[1,2] publications summarizing and explaining the results of research in this area are lacking. In the present review, solid-state fluorination of [60]fullerene, which has been successfully used[1] to synthesize the first individual compounds $C_{60}F_{36}$ and $C_{60}F_{18}$, is considered in detail.

An important problem is to perform selective polyaddition. In many cases, this problem can be solved fairly easily, if the synthesis affords compounds containing such a number of atoms that it hinders further addition for thermodynamic or kinetic reasons (for example, $C_{60}F_{48}$ or $C_{60}Br_{24}$). However, the selective synthesis of compounds containing a smaller number of functional groups requires fine adjustment of the reaction rate ratio in different steps of their successive addition to fullerene with simultaneous removal of the desired product from the reaction zone. The product can be removed by various ways, such as sublimation, evaporation, dissolution, chemical or adsorption separation (Scheme 1).

Scheme 1



Among halogen derivatives of fullerene, fluorine derivatives are most diverse. This is associated with a favorable combination of a relatively small van der Waals radius of the fluorine atoms with a rather high C—F bond energy (~300 kJ mol^{-1}). For chlorides and bromides, only compounds of composition $C_{60}X_6$, $C_{60}X_8$, and $C_{60}X_{24}$ are known, whereas all fluorides from $C_{60}F_2$ to $C_{60}F_{48}$ with even numbers of fluorine atoms are stable in the solid state, although many of these fluorides have not yet been

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isolated as individual compounds. Due to high stability of fluorinated fullerenes (fluorofullerenes), their synthesis and studies have been made possible after the synthesis of fullerenes in macroscopic amounts.

The principal results obtained in studies of the reactions of C_{60} and certain higher fullerenes with various reagents serving as fluorine sources have been covered in earlier reviews.[1,2] The present review deals primarily with the energy aspects of fullerene fluorination. The results of studies of topochemical solid-state fluorination (SSF) of [60]fullerene with inorganic variable-valence transition metal fluorides are summarized. These reactions occupy a special place because they provide a way of synthesizing such compounds as $C_{60}F_{36}$ and $C_{60}F_{18}$ with selectivity, which cannot be achieved in reactions with the direct use of elemental fluorine or other fluorinating agents. Experimental studies of solid-state fluorination primarily by mass spectrometry revealed the main characteristic features of these reactions and provided an insight into the factors responsible for their selectivity. Based on these facts, we constructed a model of solid-state fluorination, which not only explains the phenomena observed in experiments but also has a high predictive power.

2. Reactions of [60]fullerite with solid variable-valence metal fluorides

According to the available data[3—10] on the reactions of fullerene C_{60} with elemental fluorine and other fluorine-containing reagents, the reaction products generally include a broad range of fluorofullerenes of different chemical composition. Since such mixtures of compounds with similar properties are difficult to separate, the synthesis of stoichiometrically homogeneous fluorine derivatives is a rather complicated problem.

A significant progress in solving this problem was made by performing solid-state fluorination in a mixture of C_{60} with higher metal fluorides. When heated, the latter can eliminate fluorine to give lower-valent metal fluorides. Hereinafter, we will refer to these compounds as solid fluorinating agents (SFA). It appeared that these reactions can occur selectively with respect to $C_{60}F_{36}$, and this effect has been observed for the first time[11] in the reaction with MnF_3.

The synthesis of fluorine derivatives of fullerene by solid-state fluorination is based on heating a mechanical mixture of fullerite and SFA in dynamic vacuum to desired temperatures. Fluorine derivatives of C_{60} (products), whose extensive formation begins at 500—700 K, go from the mixture to the gas phase and condense on cold surfaces of the reactor. Due to sufficiently high volatility, the products cannot accumulate in the solid phase. At the same time, fullerene sublimes in insignificant amounts, and the oxidized and reduced forms of SFA remain completely in the condensed phase. The reaction products are identified on a mass spectrometer with continuous monitoring of the composition of the gas phase over the reaction mixture.

A broad range of compounds, such as FeF_3, CoF_3, AgF_2, AgF, CuF_2, CuF, K_2PtF_6, and rare-earth fluorides CeF_4 and TbF_4, were examined as fluorine sources.[12—15] The reactions of fluorides MnF_3, CoF_3, and CeF_4 with C_{60} afford predominantly $C_{60}F_{36}$.[11,12] The reaction with potassium hexafluoroplatinate selectively produces $C_{60}F_{18}$.[13] Iron trifluoride does not react with C_{60},[12] whereas TbF_4 (as the strongest SFA in this series) gives a broad range of fluorofullerenes, including compounds in which the number of fluorine atoms (n) is larger than 48, and gives also small amounts of hyperfluorinated ($n > 60$) molecules.[14]

Even the selective solid-state synthesis of fluorofullerenes is accompanied by the formation of a number of by-products of similar chemical composition in addition to the major product $C_{60}F_{2m}$. For example, $C_{60}F_{32}$, $C_{60}F_{34}$, and $C_{60}F_{38}$ along with the major product $C_{60}F_{36}$ escape from the C_{60}/MeF_3 reaction mixture (Me = Mn, Co) to the gas phase at 600—650 K.[11] In the reaction with MnF_3, the percentage of $C_{60}F_{36}$ can be much higher than 90%.

Based on the results of earlier experimental investigations,[16] the following conclusions were drawn:

1. The reaction is terminated, if the products (fluorofullerenes) are not removed from the reaction mixture in a closed reactor. Evidently, if these products become trapped between solid reagents, they retard the access of fluorine to the reaction zone. Hence, it is necessary to remove volatile products by performing the reaction in an open reactor.

2. At conventional temperatures typical of the reactions (600—650 K), fluorinated fullerenes $C_{60}F_{2m}$ are chemically inert to both each other and the starting compound C_{60}.

3. Under conditions of an open reactor, the solid-state reaction at moderate temperatures (600—650 K) proceeds readily and leads to complete decomposition of SFA in the presence of excess C_{60} or to complete consumption of the fullerene in the presence of excess SFA.

4. The reaction rate, which is monitored by measuring the formation rate of volatile products, varies rather slowly with time throughout the reaction, so that it is almost always possible to perform SSF under steady-state conditions over a long period of time. Exceptions are the very initial step and short periods after forced temperature changes.

Apparently, transport of fluorine, which is eliminated from SFA, to the zone of the reaction with C_{60} occurs efficiently enough until the reaction was completed although the reagents can be diluted with layers of decomposition products of SFA depleted of active fluorine as

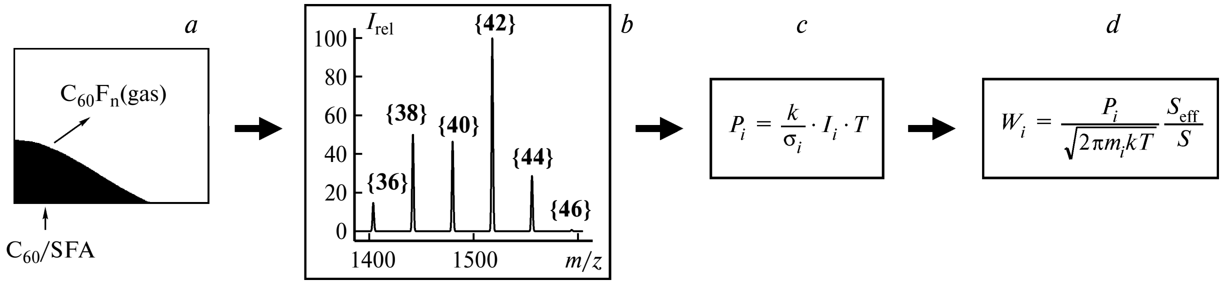


Fig. 1. Principal scheme of mass-spectrometric experiments for studying the steady-state kinetics of solid-state fluorination: *a*, reactions performed in a Knudsen cell, *b*, the mass-spectrometric analysis of gaseous products (fluorofullerenes), *c*, determination of the partial pressures of products from the intensities of ion currents, *d*, calculation of the rates of solid-state fluorination from the partial pressures of products.

the fluorine is consumed. The gas phase plays an insignificant role in the fluorine transfer because the equilibrium pressures of both molecular and atomic fluorine are low in a vapor of even relatively strong solid fluorinating agents, such as CoF_3 ($1.6 \cdot 10^{-7}$ Pa at 600 K), and these values do not correspond to the observed high reaction rates. Evidently, the reaction is maintained through chemical diffusion, which occurs due to a concentration gradient of active fluorine. As a rule, solid fluorinating agents are used as finely dispersed powders and, hence, the rate of this process can be determined by surface diffusion. High mobility of fluorine in solid metal fluorides is well known.[7,18]

To summarize, 1) the formation of fluorofullerenes occurs through successive addition of fluorine atoms released from SFA to the C_{60} carbon cage; 2) this process can be divided into three steps: (*a*) surface diffusion of fluorine to the reaction zone; (*b*) transfer of F atoms from the low-valent metal fluoride adsorbed on the surface to the chemically bound C—F state in the fluorofullerene molecule; (*c*) escape of fluorinated molecules to the gas phase.

An adequate description of solid-state fluorination can be based only on a kinetic approach. Let us consider the results of kinetic experiments, in which a complete set of reaction products was detected during the reaction of C_{60} with SFA in a Knudsen cell. These experiments made it possible to monitor the change in the composition of the products as a function of the extent of reactions with various SFA at various temperatures. The scheme of experiments is shown in Fig. 1. Fluorination of C_{60} was studied with the use of both binary transition metal fluorides (MnF_3, CoF_3) and solid fluorinating agents, *viz.*, complex lead(IV) fluorides $MgPbF_6$, $BaPbF_6$, Na_3PbF_7, and K_3PbF_7, which differ in fluorinating ability. Here, an effusion cell serves not only as a convenient reactor placed in a mass spectrometer but also as a tool allowing a quantitative description of the formation rate W_i of each product by its partial pressure $P_i = P(C_{60}F_i)$ in the gas phase over the reaction mixture. Principal data on the systems, conditions, and procedures for performing the reactions have been published earlier.[19]

3. Fluorination of C_{60} with elemental fluorine in chemically active matrices

Along with studies of solid-state fluorination, the reaction of fullerite C_{60} with elemental fluorine was investigated by mass spectrometry on introducing gas in a Knudsen cell. Experiments involved both direct fluorination of the fullerite and reactions of gaseous fluorine with a fullerite sample in the presence of a large excess (~98 mol.%) of magnesium difluoride MnF_2.[20,21] An inlet cell is shown in Fig. 2.

Manganese difluoride is chemically inert to fullerite, *i.e.*, it does not serve as a fluorine source. Hence, MnF_2 does not undergo chemical transformations and is not consumed, but it ensures high selectivity of the reaction with respect to $C_{60}F_{36}$ or $C_{60}F_{18}$. Such additives can be called chemically active matrices. Both the direct reaction with F_2 and the reactions with the use of chemically active matrices afford the same compounds with composition $C_{60}F_{2m}$. However, particular products predominate

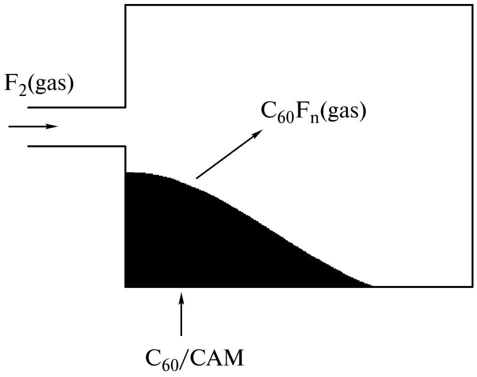


Fig. 2. Knudsen cell equipped with a capillary tube for introduction of gaseous fluorine (T = 520—720 K); CAM is a chemically active matrix.

in the reaction mixtures in the presence of chemically active matrices.

Figure 3 shows the mass spectra of the gas phase formed by fluorofullerenes upon fluorination of pure fullerite with elemental fluorine (*a*, *d*), fluorination of fullerite in chemically active matrices (*c*, *f*), and fluorination of pure fullerite with SFA (*b*, *e*). Each peak corresponds to a particular type of positive molecular ions produced by

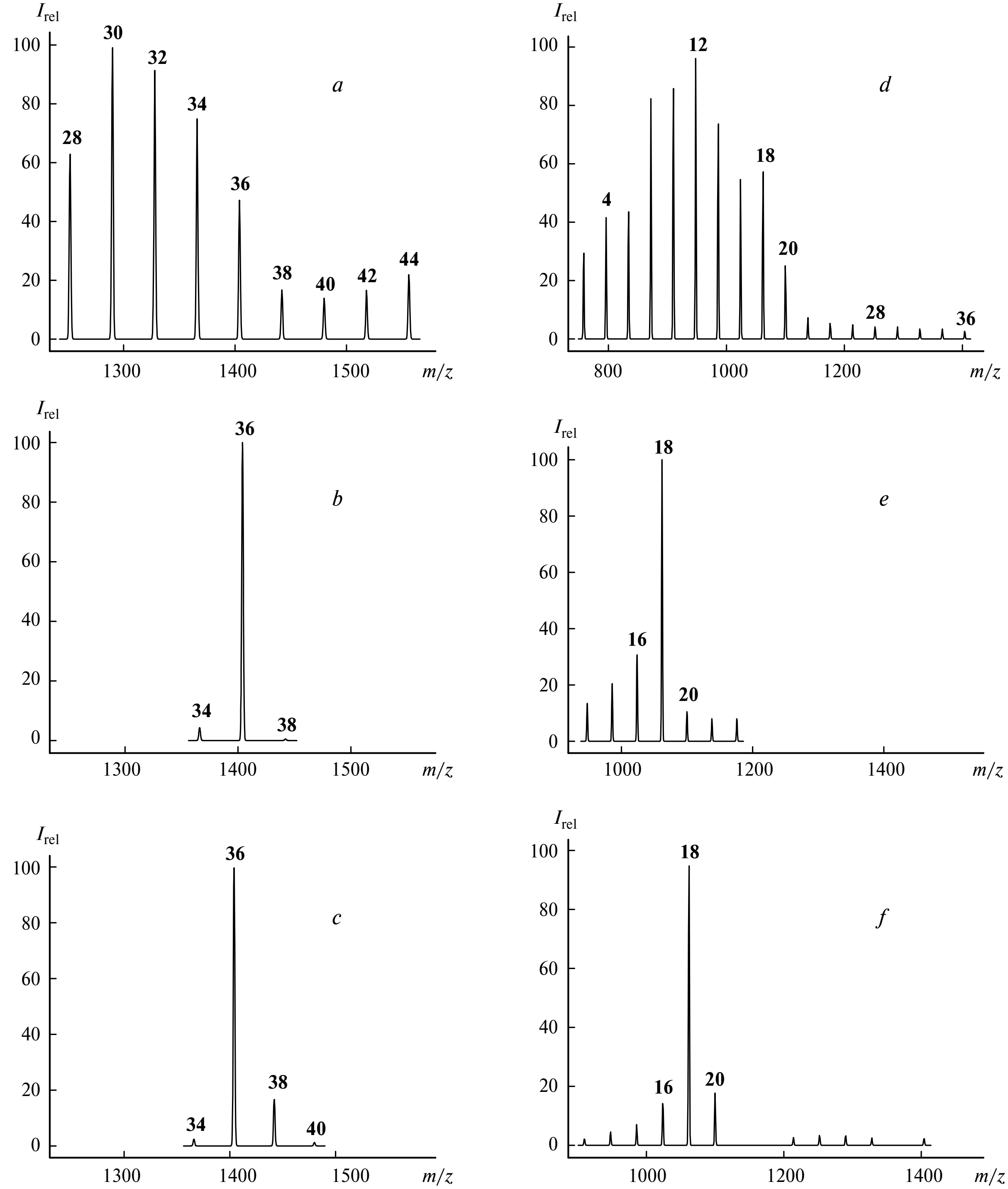


Fig. 3. Comparative data on fluorination of C_{60} under different conditions: *a*, elemental fluorine, 615 K, 8 h; *b*, the solid fluorinating agent MnF_3, 626 K, 10.3 h; *c*, the chemically active MnF_2/F_2 matrix, 615 K, 11.4 h; *d*, elemental fluorine, 720 K, 5.5 h; *e*, the solid fluorinating agent K_2PtF_6, 681 K; *f*, the chemically active MnF_2/F_2 matrix, 720 K, 8 h. Hereinafter, the numbers above the peaks correspond to the numbers of the fluorine atoms in the $C_{60}F_{2n}$ molecule.

electron impact (EI) ionization. Unlike direct fluorination giving rise to a broad range of gaseous fluorinated products, the reactions in the presence of chemically active matrices selectively produce $C_{60}F_{36}$. This result is analogous to the results of solid-state fluorination. Moreover, a comparison of the mass spectra shows that both $C_{60}F_{36}$ and $C_{60}F_{18}$ can be selectively prepared with the use of the same chemically active matrix (MnF_2) by changing the reaction temperature, whereas solid-state fluorination requires the replacement of SFA (MnF_3) by a less active reagent (K_2PtF_6). In solid-state fluorination, a change from one major product to another also occurs (see Section 7). However, under the SSF conditions, this change is much more difficult to control due to a direct relationship between the reaction temperature and the reaction rate. In the presence of chemically active matrices, an additional degree of freedom, which is gained due to independent control of the inlet gas rate and the temperature, provides this possibility.

An analogy between SSF and chemically active matrices can be accounted for by the characteristic features of fluorine transport to the reaction zone and its transfer to fullerene molecules. Actually, in all steps of solid-state fluorination, except for the very beginning, C_{60} occurs in direct contact with the SFA surface depleted of chemically bound active fluorine, *viz.*, the MnF_2 surface containing chemisorbed F atoms. The concentration of chemisorbed fluorine is maintained through diffusion of active fluorine to the reaction zone from SFA regions enriched in fluorine. In the presence of chemically active matrices, gaseous fluorine does not immediately reach fullerite grains due to the presence of a large excess of MnF_2; instead, it is initially chemisorbed on the developed surface of manganese difluoride. Then surface diffusion of gaseous fluorine to the reaction zone occurs. Hence, the conditions of solid-state fluorination are reproduced, which accounts for similar results. In the present review, the term "matrix" refers both to a chemically active matrix and SFA.

4. Selectivity and thermodynamics

The processes with the use of the above-described mode of fluorine transfer afford predominantly one particular product, whereas the reactions with F_2 and some other gaseous fluorinating agents produce, as a rule, mixtures of fluorofullerenes with various compositions.

The possible reason is that the replacement of elemental fluorine by SFA or a chemically active matrix with adsorbed fluorine gives rise to a slow step in successive fluorination, resulting in the selective formation of one particular compound (for example, $C_{60}F_{36}$) in a series from $C_{60}F_2$ to $C_{60}F_{48}$ (Scheme 2).

Scheme 2

$$C_{60} \rightarrow C_{60}F_2 \rightarrow \ldots \rightarrow C_{60}F_{2m} \rightarrow \ldots \rightarrow C_{60}F_{46} \rightarrow C_{60}F_{48}$$

The selectivity of fluorination to the $C_{60}F_{2m}$ compound in a series of compositionally similar compounds signifies that two inequalities, $P(2m) \gg P(2m - 2)$ and $P(2m) \gg P(2m + 2)$, are simultaneously satisfied for the partial pressures of the products containing $2m - 2$, $2m$, and $2m + 2$ fluorine atoms. The selectivity conditions can be stated as a need to change the sign of the Gibbs energy for two successive ($\delta m = 1$) reactions from minus (in the reaction yielding $C_{60}F_{2m}$) to plus (in the reaction yielding $C_{60}F_{2m+2}$):

Scheme 3

$$C_{60}F_{2m-2}(\text{gas}) + 2\ \text{MeF}_n(\text{cryst}) = C_{60}F_{2m}(\text{gas}) + 2\ \text{MeF}_{n-1}(\text{cryst}), \qquad (3a)$$

$$C_{60}F_{2m}(\text{gas}) + 2\ \text{MeF}_n(\text{cryst}) = C_{60}F_{2m+2}(\text{gas}) + 2\ \text{MeF}_{n-1}(\text{cryst}), \qquad (3b)$$

$$K_{2m} = [P(2m + 2)/P(2m)][a(\text{MeF}_{n-1})^2/a(\text{MeF}_n)^2],$$

$$\Delta_r G^\circ(2m) = -RT\ln K_{2m},$$

where the equilibrium constants K_{2m} are expressed in terms of the partial pressures P and the activities a.

If the Gibbs energis of the reactions are approximately equal in absolute value, the selective formation of $C_{60}F_{2m}$ can be achieved already at $|\Delta_r G^\circ(3)|$ of as less as 5—6 kJ mol^{-1}, *i.e.*, $\Delta_r G^\circ(3a) = -6$ kJ mol^{-1} and $\Delta_r G^\circ(3b) = +6$ kJ mol^{-1} (Fig. 4).

Figure 4,*a* shows the compositions of adjacent products corresponding to the situation, where the Gibbs energies of the reactions (3) are equal in absolute value (6 kJ mol^{-1}). Figure 4,*b* corresponds to the Gibbs energies of −10 and +2 kJ mol^{-1} for the reactions (3a) and (3b), respectively (see Scheme 3).

It should be noted that the difference $\delta\Delta_r G^\circ$ between these energies corresponds to the reaction in the gas phase

$$C_{60}F_{2m-2}(\text{gas}) + C_{60}F_{2m+2}(\text{gas}) = 2\ C_{60}F_{2m}(\text{gas}), \qquad (4)$$

in which the change in the entropy $\Delta_r S^\circ$ can reasonably be ignored. Then we have:

$$\delta\Delta_r G^\circ(4) = 2D_{CF}(2m - 2) - 2D_{CF}(2m) = 2\delta D_{CF}, \qquad (5)$$

where $D_{CF}(2m)$ is the average energy of binding of the F atom to the $C_{60}F_{2m}$ molecule in the reaction giving rise to the $C_{60}F_{2m+2}$ molecule. Therefore, a negative jump in the energy D_{CF} of about 10—12 kJ mol^{-1} on going from

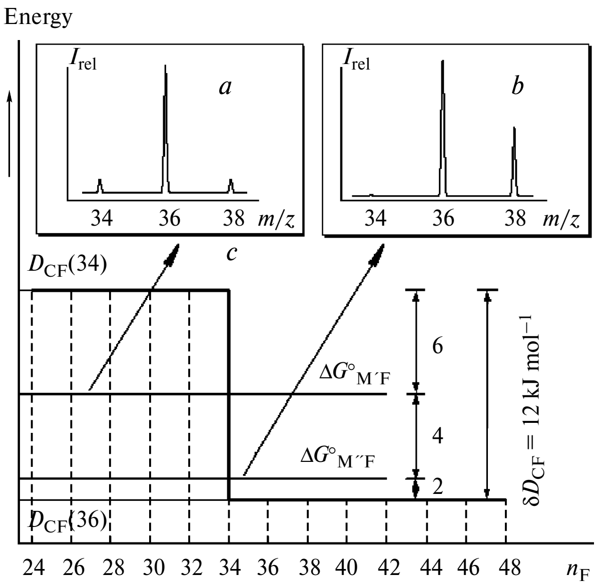


Fig. 4. Selectivity of solid-state fluorination from the thermodynamic point of view; n_F is the number of F atoms.

the $C_{60}F_{2m}$ molecule to $C_{60}F_{2m+2}$ is sufficient for the selective formation of the $C_{60}F_{2m}$ product.

The available experimental data demonstrate that, although the energies of the C—F bonds in the compositionally different fluorofullerene molecules differ only slightly, the actual energy difference δD_{CF} between $C_{60}F_{34}$ and $C_{60}F_{36}$ is most likely larger than the above values. In early studies,[9,10] almost equal estimates were obtained for the D°(C—F) energies (365±2 kJ mol^{-1}) by examining the gas-phase equilibria involving $C_{60}F_{2m}$ for the overall series of the molecules. According to the more recent and, apparently, more reliable data obtained in studies of $C_{60}F_{36}$ [22] and $C_{60}F_{48}$,[23] by combustion calorimetry, the average C—F bond energy $\langle D°_{CF}\rangle$ in the $C_{60}F_{36}$ molecule is 295 kJ mol^{-1}, whereas the average energy of 265 kJ mol^{-1} is required for abstracting the first twelve fluorine atoms from the $C_{60}F_{48}$ molecule. Assuming that the individual energies change smoothly in the series of the $C_{60}F_2$—$C_{60}F_{34}$ and $C_{60}F_{38}$—$C_{60}F_{48}$ molecules, the actual difference $\Delta D°_{CF} = 0.5[D°(C_{60}F_{34} - 2\ F) - D°(C_{60}F_{36} - 2\ F)]$ can be 15—20 kJ mol^{-1}, and the limiting value is 30 kJ mol^{-1}. Taking into account that, due to high stability of $C_{60}F_{36}$, the largest jump in the C—F bond energies can be expected on going from $C_{60}F_{36}$ to $C_{60}F_{38}$ we reached the conclusion that a weak difference in the C—F bond energies in fluorofullerenes cannot prevent the appearance of selectivity in solid-state fluorination. In this case, the energies of the reactions (3), which are completely determined by the difference in the bond energies $D_{CF}(2m)$, can serve as a convenient criterion for choosing an appropriate solid fluorinating agent.

Nevertheless, selectivity of SSF cannot be accounted for by thermodynamic factors. Actually, taking into account the need to change the sign of $\Delta_r G°(3)$ if a chemical equilibrium is established in the reactions (3), it can be stated that the energy of abstraction $D_{MF} = \Delta H°_0(MeF_{n-1} - F)$ of the first F atom from the SFA molecule should be in the middle of a narrow range (<30 kJ mol^{-1}) determined by the difference between $D_{CF}(2m - 2)$ and $D_{CF}(2m)$. However, the $C_{60}F_{36}$ compound is selectively formed in reactions involving SFA, which differ rather substantially in fluorinating ability. For example, the difference in the enthalpies in the reactions $MeF_3 = MeF_2 + F$ involving CoF_3 and MnF_3 estimated in different studies varies in a range of 90—100 kJ mol^{-1}. The ratios of the $C_{60}F_{34}$, $C_{60}F_{36}$, and $C_{60}F_{38}$ products are within one order of magnitude. If the system is at equilibrium, this ratio is realistic for a case where a change in the enthalpy in these reactions is no higher than 10 kJ mol^{-1}. Moreover, mass spectrometric studies provided direct evidence that under the conditions of solid-state fluorination, the equilibria (4) are not established.[16,24]

Let us attempt to describe solid-state fluorination in terms of a kinetic scheme. This approach is based on consideration of the activation energies of elementary steps in successive additions of fluorine atoms to the carbon cage. The step (*b*) corresponding to the transfer of fluorine atoms from SFA to fullerene C_{60} is taken as an elementary step (see Section 2). This step together with the step (*c*) can be represented by the following scheme:

$$C_{60}F_n(gas) + \{F\}[SFA] \rightarrow C_{60}F_{n+1}(gas) + [SFA]. \qquad (6)$$

In this scheme, the braces enclose the fluorine atoms in the chemisorbed state on the SFA surface, and the brackets enclose the compound in the solid state. The region, where fluorinated molecules are continuously generated (the reaction zone), is a thin layer at the grain interface of the reagents, *viz.*, C_{60} and SFA. At each instant of time, fluorofullerene molecules with different chemical compositions are formed in the reaction mixture. These molecules cannot form a crystalline phase due to extensive sublimation.

5. Characteristic features of energetics of solid-state fluorination and activation barriers

It is known that there is a particular relation between the reaction rates and enthalpies. A knowledge of the quantitative relations between these parameters opens up possibilities of using the thermodynamic characteristics of the reactions to estimate their relative rates. Generally, this holds for a combination of these reactions (hereinafter, these reactions are denoted by the indices *i*), which are derived from each other by replacing the functional group responsible for the reaction with an analogous group in one of the reagents.

The reactions (3) or (6) represent such a one-parameter sequence. The number of fluorine atoms in the fluorofullerene molecule involved in the reaction can be used as the parameter. This allows us to employ a correlation approach analogous to the so-called Bell—Evans—Polanyi (BEP) model, which is well known in organic chemistry.[25]

The BEP model is based on the principle of "independence" of the dissociation and formation of chemical bonds in elementary reactions. The "independence" assumes that the plot of the energy of the starting compounds—products system *vs.* the common reaction coordinate, which describes the course of the reaction, can be represented as two independent curves. One curve represents the dependence of the energy on the bond extension (an increasing curve), whereas another curve describes the dependence of the energy on the bond contraction (a decreasing curve). The point of intersection of the curves corresponds to a transition state and determines the activation energy.

Families of reactions, which obey the BEP principle, are characterized by the linear dependence of the activation energy E_{ai} on the enthalpy ΔH_i:

$$E_{ai} = A + B\Delta H_i, \qquad (7)$$

the latter should only slightly vary within a family.

The coefficient B tends to decrease with increasing absolute value of ΔH. Hence, for two families of reactions with substantially different enthalpies, the stronger dependence of E_{ai} on ΔH_i will be observed in the family, where the enthalpies are close to zero, because even a small shift of ΔH_i will lead to a substantial change in the activation energy. This concept provides the basis of the Brown selectivity relationship for aromatic substitution.

The possible Evans—Polanyi curves for two pairs of the elementary reaction steps (6) of fluorine transfer to adjacent fluorofullerenes, which are involved in reactions with two arbitrary solid fluorinating agents $M^{I}F_n$ and $M^{II}F_k$ having substantially different fluorinating abilities, were described in the study.[16] It was demonstrated[16] that, in terms of the BEP concept, the differences in the activation energies for successive steps in these two families of reactions can be substantially different even if the differences in the enthalpy of the reactions within each family are equal.

If the BEP principles are applicable to solid-state fluorination of fullerene, the requirement for a change in the sign of the Gibbs energy in the corresponding step of the addition reaction sequence is not a necessary condition for the selective formation of the desired product. It makes imperative that a decrease in the Gibbs energy in this fluorination step should be accompanied by an increase in the activation energy larger than that in other fluorination steps. The selective synthesis of the individual compounds $C_{60}F_{18}$ and $C_{60}F_{36}$ by solid-state fluorination is associated with the fulfillment of this condition, which is not met in fluorination with elemental fluorine.

Taking into account the specific features of fluorine derivatives of fullerene associated with weak differences in the C—X bond energies in the $C_{60}F_{2m}$ series, it can be stated that the directed synthesis of fluorofullerenes with a specified stoichiometry can afford the desired product only when the difference in the thermochemical properties of fluorofullerenes is extensively used.

The energy approach in terms of the BEP model provides an insight into a nonselective character of direct fluorination of fullerene with molecular fluorine. Actually, the dissociation enthalpy of the F_2 molecule is approximately 150 kJ mol^{-1} and, in combination with $D_{C_{60}F_{34}}$ = 295 kJ mol^{-1} and $D_{C_{60}F_{36}}$ = 265 kJ mol^{-1} (see Section 4), indicates a pronounced exothermic character (≅ –280 kJ mol^{-1}) of the addition of two atoms to both the $C_{60}F_{34}$ and $C_{60}F_{36}$ molecules. Hence, the activation energies in individual steps weakly depend on the enthalpy, and even the largest difference (δD_{CF}) of 20—30 kJ mol^{-1} between $D_{C_{60}F_{34}}$ and $D_{C_{60}F_{36}}$ is too small and does not lead to substantial changes in the activation energy on going from one step of the $C_{60}F_{2m} + 2\ F = C_{60}F_{2m+2}$ reaction to another one. On the contrary, a decrease in the average enthalpy to ≅ –50 kJ mol^{-1} in the reactions with MnF_3 or F_2 in the presence of an MnF_2 matrix with the same difference δD_{CF} leads not only to a total increase in the activation energy but also to a selective increase in E_a of the step $C_{60}F_{36} + 2\ F = C_{60}F_{38}$ due to a substantially stronger dependence of E_a on ΔH according to Eq. (7). Both diagrams (Fig. 5) are characterized by equal differences in the reaction enthalpies corresponding to the same steps, whereas the absolute values of the enthalpies are substantially different. The reaction with MnF_3 is selective to the $C_{60}F_{36}$ product, whereas the reaction with gaseous fluorine affords a broad range of products (see Fig. 5, *c*, *d*). In the first reaction (see Fig. 5, *c*), the differences in the activation energy were evaluated by processing the experimental data on SSF in terms of the kinetic model. In the second reaction (see Fig. 5, *d*), the corresponding differences were estimated by a numerical experiment, in which the activation energies were chosen in such a way as to reproduce the product distribution observed in the mass spectrometric experiment on introducing fluorine into the reaction.

Our approach suggests the energy of fluorine transfer from SFA to fullerene as a measure for choosing reagents to perform the selective synthesis of fluorofullerenes. In searching for the desired SFAs, it is recommended that the experimental energies of bond cleavage in molecules be used as a measure. This principle may be useful for preparing not only fluorine derivatives but also other individual fullerenes.

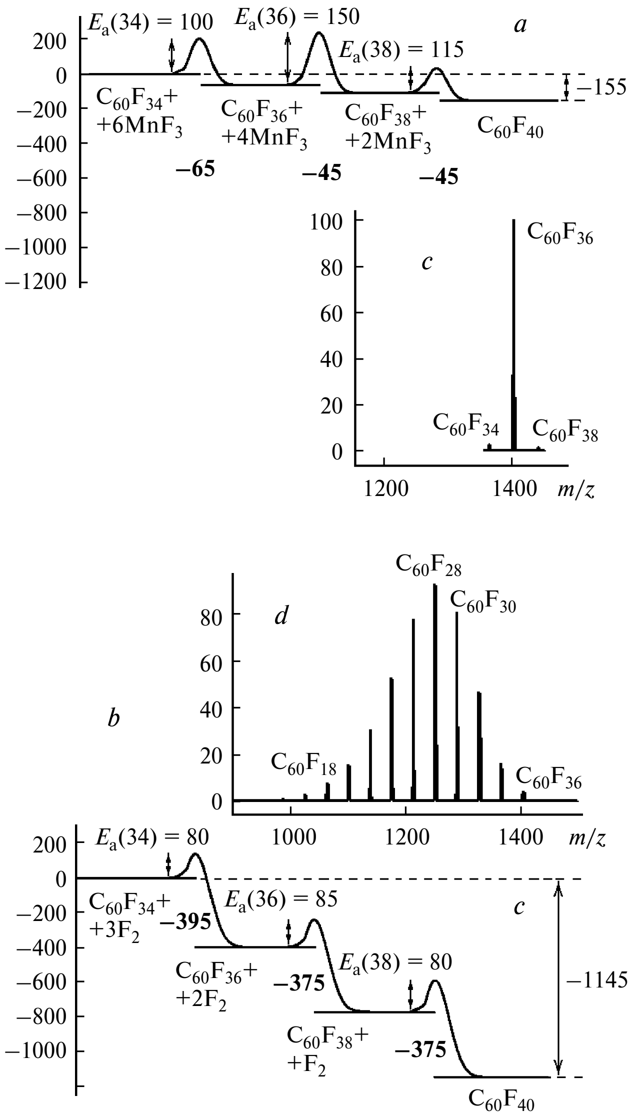


Fig. 5. Effect of the enthalpies of elementary steps of fluorination of C_{60} on the activation energy: *a*, a solid-state reaction with MnF_3 characterized by low enthalpy, *b*, a reaction with elemental fluorine characterized by high enthalpy; the distribution of gaseous reaction products is shown in the insets *c* and *d*.

6. Selectivity and kinetics

The model and its mathematical apparatus have been described in detail in our earlier publications.[19,24] From the point of view of the formal kinetics, the steps *b* and *c* (see Scheme (6)) in the overall fluorination sequence starting with C_{60} and ending with $C_{60}F_{48}$ are of most interest (Scheme 4).

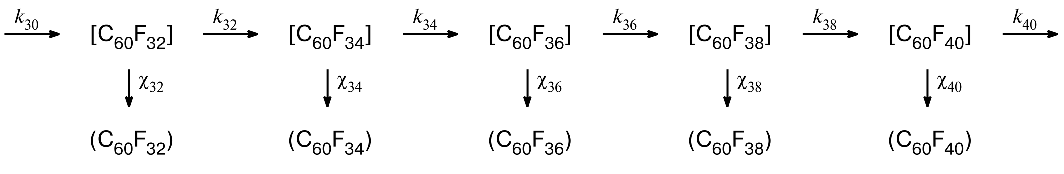
In this scheme, the brackets and parentheses enclose compounds in the solid and gas phases, respectively, k_i are the reaction rate constants (6), χ_i are the proportionality coefficients between the concentrations C_i of fluorofullerenes in the solid state and their vaporization rates v_i per unit surface area: $v_i = \chi_i C_i$. These coefficients can be referred to as "sublimation rate constants," assuming first-order reactions. The concentrations C_i signify the molecular densities of $C_{60}F_i$ in the microscopically thin reaction zone.

The key question is how fluorine is transferred from SFA to fullerene molecules. In our model, this transfer is described as "desorption" of fluorine from the SFA surface followed by the addition to the $C_{60}F_n$ molecules, which are in contact with the starting fullerite crystals and can either escape to the gas phase or be subjected to deeper fluorination. The term "desorption" is enclosed in quotation marks because intermediate fluorine transfer to the gas phase does not occur. Many details of the mechanism of fluorine transfer associated, for example, with a particular form of existence of fluorine on the surface or with charge transfer are insignificant for the phenomenological description and remain beyond the scope of the model.

This sequence of similar reactions is characterized, first, by an unusual length of the sequence, and, second, by the occurrence of competitive processes in each step associated with distillation of volatile products. When comparing the model representation with the experimental data, we extensively used the similarity of the reactions. This suggests that many parameters, which characterize both the reactions and the compounds involved in these reactions, can smoothly vary from step to step in the reaction sequence. Since the number of fluorine atoms in highly fluorinated $C_{60}F_i$ molecules changes relatively little upon the addition of the next fluorine atom, the differences in certain values (for example, in volatility) for the "adjacent" molecules can be ignored.

The kinetics of the reactions proceeding according to Scheme 4 is described by a closed system of differential equations. Steady-state solutions of this system for the relative partial pressures of fluorofullerenes were obtained and analyzed in accordance with the character of reactions (formation of products in the gas phase) and the

Scheme 4



$$\begin{tikzcd}
{} \arrow[r, "k_{30}"] & {[C_{60}F_{32}]} \arrow[r, "k_{32}"] \arrow[d, "\chi_{32}"] & {[C_{60}F_{34}]} \arrow[r, "k_{34}"] \arrow[d, "\chi_{34}"] & {[C_{60}F_{36}]} \arrow[r, "k_{36}"] \arrow[d, "\chi_{36}"] & {[C_{60}F_{38}]} \arrow[r, "k_{38}"] \arrow[d, "\chi_{38}"] & {[C_{60}F_{40}]} \arrow[r, "k_{40}"] \arrow[d, "\chi_{40}"] & {} \\
 & (C_{60}F_{32}) & (C_{60}F_{34}) & (C_{60}F_{36}) & (C_{60}F_{38}) & (C_{60}F_{40}) &
\end{tikzcd}$$

course of the reactions studied experimentally.[19,24] It can be seen that the partial pressure ratios of the products in the cell differ from their concentration ratios in the reaction zone by the multipliers

$$q_i = P_{i-1}{}^0/P_i{}^0 \qquad (8).$$

Here we give only the final equation, which was derived using a common technique, when all concentrations are initially assumed to be constant, but some of them are then treated as parameters slowly varying with time:

$$\frac{P_{i-1}}{P_i} = \frac{P^0_{i-1}}{P^0_i}\frac{C_{i-1}}{C_i} = \frac{P^0_{i-1}}{P^0_i}\frac{k_i}{k_{i-1}}\left(1 + \frac{\chi_i}{k_iC_{\mathrm{F}}}\right) = q_iu_i(1 + \xi_i). \quad (9)$$

In this equation, $C_{\mathrm{F}} = f(t)$ is the current surface fluorine concentration in the reaction zone. The following notations are also used: $u_i = k_i/k_{i-1}$, $\xi_i = \chi_i/k_iC_{\mathrm{F}}$. These values play the key role in the chemical composition distribution of the resulting fluorofullerenes.

The numerical values of these multipliers, which are required for the practical use of Eqs (9), can be calculated from the experimental data on the saturated vapor pressure of fluorofullerenes.[26,27]

The concentration C_{F} serves as the above-mentioned slowly varying parameter. This parameter can be used to study the effect of the active fluorine concentration in the reaction zone on the relative yields of the products under isothermic conditions. The data given in Table 1 provide an insight into the real changes in C_{F} with time in selected solid-state fluorination reactions.

In solid-state fluorination reactions, it often occurs that, under particular temperature conditions or at a particular step, the formation of the major products (one or two) is accompanied by the formation (although in substantially smaller amounts) of by-products, *viz.*, fluorofullerenes, similar in fluorine content to the major products. We arbitrarily call this situation for three successive reaction products the *local selectivity.* Let us consider the

Table 1. Overall product flows and changes in the active fluorine concentration with time in isothermic regions of the reactions of C_{60} with solid fluorinating agents

C_{60}(fcc)[a]/MnF_3			C_{60}(fcc)/CoF_3			C_{60}(fcc)/$MgPbF_6$		
t/min	$\Sigma\nu_{\mathrm{F}}$[b]	$C_{\mathrm{F}}(t)/C_{\mathrm{F}}(0)$[c]	t/min	$\Sigma\nu_{\mathrm{F}}$	$C_{\mathrm{F}}(t)/C_{\mathrm{F}}(0)$	t/min	$\Sigma\nu_{\mathrm{F}}$	$C_{\mathrm{F}}(t)/C_{\mathrm{F}}(0)$
	$T = 626$ K			$T = 653$ K			$T = 593$ K	
620	$2.19 \cdot 10^{17}$	100.0	700	$1.28 \cdot 10^{18}$	100.0	235	$4.07 \cdot 10^{17}$	100.0
630	$2.19 \cdot 10^{17}$	100.3	740	$5.90 \cdot 10^{17}$	47.1	280	$1.99 \cdot 10^{17}$	49.0
660	$1.75 \cdot 10^{17}$	79.9	760	$4.75 \cdot 10^{17}$	38.3	310	$1.59 \cdot 10^{17}$	39.2
675	$1.55 \cdot 10^{17}$	71.0	770	$3.91 \cdot 10^{17}$	31.8	345	$1.13 \cdot 10^{17}$	27.9
750	$9.64 \cdot 10^{16}$	44.2	790	$3.43 \cdot 10^{17}$	28.3	375	$9.02 \cdot 10^{16}$	22.1
772	$8.76 \cdot 10^{16}$	40.2	805	$2.91 \cdot 10^{17}$	24.2	425	$6.78 \cdot 10^{16}$	16.6
780	$8.47 \cdot 10^{16}$	38.8	830	$1.04 \cdot 10^{17}$	8.9	480	$1.41 \cdot 10^{17}$	34.6
810	$7.67 \cdot 10^{16}$	35.2	905	$4.58 \cdot 10^{16}$	4.0	495	$1.41 \cdot 10^{17}$	34.6
845	$6.58 \cdot 10^{16}$	30.2	1010	$3.35 \cdot 10^{16}$	3.0			
848	$6.43 \cdot 10^{16}$	29.5	1025	$3.18 \cdot 10^{16}$	2.8		$T = 653$ K	
	$T = 663$ K			$T = 703$ K		590	$2.66 \cdot 10^{17}$	100.0
1070	$5.83 \cdot 10^{17}$	100.00	1107	$2.18 \cdot 10^{15}$	100.0	605	$2.39 \cdot 10^{17}$	90.0
1115	$2.36 \cdot 10^{17}$	58.32	1110	$4.29 \cdot 10^{16}$	94.0	650	$1.34 \cdot 10^{17}$	52.2
1120	$1.53 \cdot 10^{17}$	41.36	1115	$3.32 \cdot 10^{16}$	72.3	675	$1.07 \cdot 10^{17}$	41.8
1125	$1.28 \cdot 10^{17}$	34.43	1120	$1.41 \cdot 10^{15}$	66.6	705	$9.23 \cdot 10^{16}$	36.8
1145	$5.16 \cdot 10^{16}$	16.18	1135	$1.15 \cdot 10^{15}$	61.0	735	$7.57 \cdot 10^{16}$	30.8
1165	$3.28 \cdot 10^{16}$	10.62	1150	$2.03 \cdot 10^{16}$	44.3			
1190	$1.39 \cdot 10^{16}$	4.62	1160	$1.72 \cdot 10^{16}$	38.3		$T = 709$ K	
1200	$9.00 \cdot 10^{15}$	2.99	1165	$1.52 \cdot 10^{16}$	33.9	935	$3.39 \cdot 10^{17}$	100.0
1210	$5.76 \cdot 10^{15}$	1.91	1185	$7.30 \cdot 10^{15}$	16.3	945	$1.80 \cdot 10^{17}$	53.2
1230	$2.82 \cdot 10^{15}$	0.93	1200	$4.26 \cdot 10^{15}$	9.5	951	$5.98 \cdot 10^{16}$	17.7
1260	$5.31 \cdot 10^{14}$	0.18	1215	$3.16 \cdot 10^{15}$	7.1	975	$1.40 \cdot 10^{16}$	4.1
1275	$2.89 \cdot 10^{14}$	0.09	1235	$2.01 \cdot 10^{15}$	4.5	990	$4.87 \cdot 10^{15}$	1.4
1315	$2.07 \cdot 10^{14}$	0.07	1265	$8.39 \cdot 10^{14}$	1.9	1005	$3.25 \cdot 10^{15}$	1.0

[a] A face-centered cubic (fcc) lattice.

[b] The fluorine atom flow per unit reaction surface area calculated from the overall flow of fluorinated products to the gas phase/atom m^{-2} s^{-1}.

[c] The point of time corresponding to the beginning of the column was taken as the reference point; the concentration ratio was taken with a coefficient of 100.

possibility of its occurrence according to the main equation (9).

The rate constants of elementary steps of the successive fluorine addition are included in Eq. (9) as $u_{ij} = k_i/k_j$. A low value of this ratio signifies the presence of a slow step in the reaction sequence of successive fluorine addition. Evidently, this is a necessary condition for a particular product to be formed as the major one. Besides, the relative formation rates of the products are controlled to a large degree by the dimensionless *combined* parameters ξ_i, whose physical meaning is that they are the ratios of the sublimation rate of the $C_{60}F_i$ product from the mixture to the rate of its deeper fluorination.

The model mass spectra (Fig. 6), which are constructed at substantially different ξ, illustrate the influence of this parameter on the distribution of the products. For convenience, fluorination of C_{60} was simulated at *equal* activation energies. In this case, the parameter ξ is a function of the fluorine concentration C_F only. The initial value of the latter was chosen in accordance with reasonable theoretical estimates. Simulation was carried out with the use of the real saturated vapor pressures of the reaction participants. The temperature of 626 K was chosen because it is close to the optimum temperature for the synthesis of fluorine derivatives of C_{60} in reactions with MnF_3. An increase in ξ caused by a decrease in the fluorine concentration C_F leads to a shift of the composition of the gaseous mixture to products with a lower fluorine content.

Let us consider what conditions should be met for local selectivity. The selective formation of the $C_{60}F_n$ compound with respect to the nearest neighbors $C_{60}F_{n-1}$ and $C_{60}F_{n+1}$ means that the following conditions are fulfilled:

$$\frac{P_{n-1}}{P_n} = \frac{k_n}{k_{n-1}}\cdot(1+\xi_n) = \frac{k_n}{k_{n-1}} + \frac{\chi_n}{k_{n-1}C_F} << 1,$$

$$\xi_n = \chi_n/(k_nC_F), \tag{10}$$

$$\frac{P_n}{P_{n+1}} = \frac{k_{n+1}}{k_n}\cdot(1+\xi_{n+1}) = \frac{k_{n+1}}{k_n} + \frac{\chi_{n+1}}{k_nC_F} >> 1,$$

$$\xi_{n+1} = \chi_{n+1}/(k_{n+1}C_F). \tag{11}$$

When deriving the above inequalities, we ignored the multipliers q_n and q_{n+1} which are close to unity, in Eqs (9) taking into account that the products are similar in fugacity. For the same reason, χ_n and χ_{n+1} can be assumed to be equal.

Evidently, Eq. (10) will be fulfilled only if both dimensionless terms are much smaller than unity:

$$k_n/k_{n-1} \ll 1, \tag{12a}$$

$$\chi_n/(k_{n-1}C_F) \ll 1. \tag{12b}$$

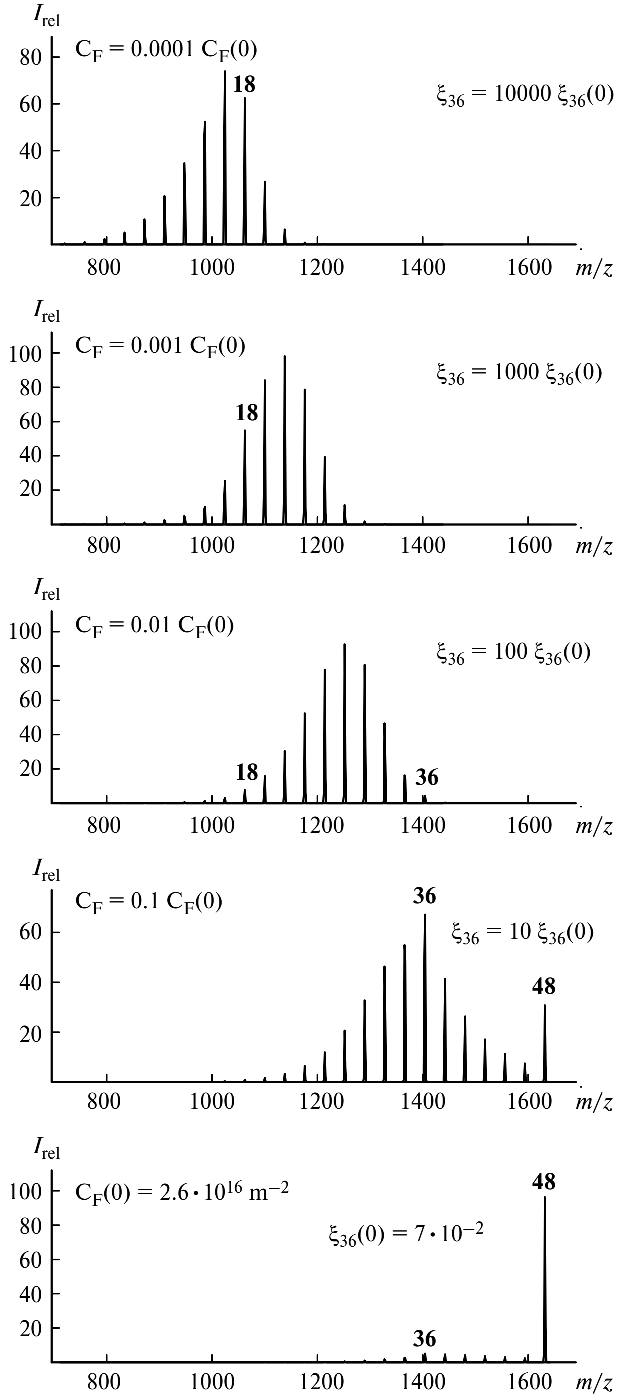


Fig. 6. Model mass spectra of fluorofullerenes prepared by fluorination of C_{60} with elemental fluorine at the equal activation energies $E_0 = ... = E_{46} = 135$ kJ mol^{-1} and at different concentrations of active fluorine; $T = 626$ K. The numbers above the peaks indicate the numbers of fluorine atoms in the $C_{60}F_{2m}$ molecule.

The inequality (12a) reflects the existence of a slow step in the reaction sequence presented in Scheme 4. The physical meaning of the inequality (12b) becomes clear when both its sides are multiplied by k_{n-1}/k_n, after which this inequality assumes the form

$$\chi_n/(k_n C_F) \ll k_{n-1}/k_n. \qquad (13)$$

The latter inequality means that the ratio of the sublimation rate of the compound formed selectively to the rate of its further fluorination should be small compared to the ratio of the rate constants of the fast (fluorination of $C_{60}F_{n-1}$) and slow (fluorination of $C_{60}F_n$) steps.

Therefore, both the jump in the rate constant of fluorination in one of the steps and the existence of a particular relationship between the terms involved in the combined parameter ξ_n are the necessary (but not sufficient) conditions for local selectivity. The inequalities (12) will be referred to as the *main selectivity conditions.* If these conditions are met, the formation of a product with the index n (the central product in the triplet of the products under consideration) becomes much more favorable than the formation of its precursor ($i = n - 1$).

To find the conditions for the fulfillment of the inequality (11), which assumes also a rather low formation rate of the next product $C_{60}F_{n+1}$, it is necessary to consider two situations.

1. The $C_{60}F_{n+1}$ compound much more rapidly reacts with active fluorine than the kinetically most stable $C_{60}F_n$ compound, *i.e.*, $k_{n+1}/k_n \gg 1$. In this case, the inequality is fulfilled regardless of the combined parameter ξ_n, *i.e.*, regardless of the ratio of the distillation to fluorination rates. Hence, the selectivity is provided at all sublimation rates.

2. The $C_{60}F_{n+1}$ compound is equally or even less reactive than $C_{60}F_n$, *i.e.*, $k_{n+1}/k_n \le 1$. Then, the condition (11) is met only at rather high distillation rates. Since too high sublimation rates can lead to violation of the main selectivity conditions, a balance between the sublimation and fluorination rates is required. This balance is mathematically described by the double inequality:

$$1 \ll \chi_n/(k_n C_F) \ll k_{n-1}/k_n. \qquad (14)$$

The parameters k_{n-1}/k_n and ξ_n responsible for selectivity can vary with temperature and time to a different degree during the reaction, resulting in a loss of or, on the contrary, in an increases in selectivity.

The proposed model provides also a possibility for determining the *relative* reaction rate constants of different fluorination steps from experimental data. Assuming the Arrhenius temperature dependence of the rate constants, the *differences* $\delta_i = E_i - E_{i-1}$ can be evaluated by statistical processing of an overdetermined equation system derived on the basis of the relationships (9) in terms of activation energies. This form of steady-state solutions of the kinetic equations has the advantage that the differences δ_i, unlike the corresponding reaction rate ratios, are temperature independent. This enables one to include points measured at different temperatures in the data processing. By contrast, the parameters ξ_i depend on both the temperature and time because the fluorine concentration C_F changes during the reaction.

Experimental data processing requires the involvement of the ratios of the preexponential coefficients as input parameters. However, it is impossible to perform a completely justified theoretical evaluation of these parameters because of the lack of the molecular constants for the overwhelming majority of fluorofullerenes. To overcome this problem, we invoked the similarity of all steps of the reaction sequence under consideration assuming that the parameters A_i differ little for fluorofullerenes with similar numbers of fluorine atoms.

The preexponential coefficients for practical calculations were evaluated based on the concepts of the activated complex theory. All values are close to unity. A smooth change in the ratio of the preexponential coefficients in the series of $C_{60}F_{2m}$ can be violated due to the different symmetry numbers assigned to fluorofullerene molecules. This factor can be taken into account for compounds in which the number of fluorine atoms is 0, 2, 18, 20, 36, or 48. For these compounds, experimental data on the geometric structures of the molecules are available.

The differences in the activation energy (Table 2) are indicative primarily of high kinetic stability of the C_{60}, $C_{60}F_{18}$, and $C_{60}F_{36}$ compounds. For this reason, these compounds are obtained as the major products in the overwhelming majority of solid-state fluorination reactions and reactions in the presence of chemically active matrices. These facts agree well with the structural features of the molecules. The initial step of fullerene fluorination is characterized by the highest activation energy, which is associated with higher stability of its π-electron system. Already the addition of the first two fluorine atoms at the double bond irreversibly disrupts this symmetrical electronic structure, resulting in an increase in the reactivity of the molecules in further fluorination. The next "stability island" is observed for fluorofullerenes, in which the number of fluorine atoms at the carbon cage is 18 or 36. In the former molecule,[28] all 18 fluorine atoms are bound at the same hemisphere of C_{60}, due to which the hemisphere of the cage free of fluorine is noticeably flattened to form a benzene-like ring in its center, which contributes to stabilization of the molecule. The feature of the $C_{60}F_{36}$ molecules, whose most abundant isomer is characterized by the C_3 symmetry, is that the molecule contains three isolated benzene-like rings and three isolated double bonds.[29,30] Hence, the addition reaction requires that a higher energy barrier be overcome. For reactions with various solid fluorinating agents, the highest jump is observed in the $C_{60}/BaPbF_6$ reaction, which is in agreement with the fact that this reagent provides the highest selectivity (>98%) in the synthesis of $C_{60}F_{36}$. Cobalt trifluoride, which is the strongest SFA

Table 2. Differences $\Delta_{i/j} = E_j - E_i$ (kJ mol^{-1}) for the reactions of C_{60} with solid fluorinating agents

$\Delta_{i/j}$	$BaPbF_6$	$MgPbF_6$	Na_3PbF_7	K_3PbF_7	MnF_3	CoF_3
$\Delta_{00/18}$	—	−46.2±0.4	−57.8±0.3	−71.8±0.8	−24.7±2.3	−44.8±2.9
$\Delta_{18/32}$	—	−36.2±0.4	−37.1±0.4	—	−65.9±1.4	−51.3±1.5
$\Delta_{18/34}$	—	—	—	−27.8±0.8	−54.5±1.6	−41.4±3.0
$\Delta_{18/20}$	—	−27.1±0.6	—	—	—	—
$\Delta_{20/22}$	—	−7.8±0.5	—	—	—	—
$\Delta_{22/24}$	—	−3.2±0.7	—	—	—	—
$\Delta_{24/26}$	—	2.0±0.4	—	—	—	—
$\Delta_{26/28}$	—	−0.5±0.3	—	—	—	—
$\Delta_{28/30}$	—	−2.9±0.4	—	—	—	—
$\Delta_{30/32}$	—	−4.3±0.6	—	—	—	—
$\Delta_{32/34}$	—	4.9±0.8	9.4±0.4	—	7.3±0.9	10.0±2.3
$\Delta_{34/36}$	68.6±1.2	51.3±0.7	45.3±1.9	36.6±1.7	51.1±3.2	30.3±1.6
$\Delta_{36/38}$	−20.2±2.8	−31.7±0.3	—	—	−35.2±2.5	−2.9±0.7
$\Delta_{38/40}$	—	—	—	—	—	3.1±0.5
$\Delta_{40/42}$	—	—	—	—	—	10.3±0.6
$\Delta_{42/44}$	—	—	—	—	—	16.4±1.7

studied by us, assists in decreasing the difference in the activation energy, resulting in the formation of a set of fluorofullerenes $C_{60}F_{36}$—$C_{60}F_{46}$ in early reaction steps.

7. Comparison of theory with experiment

7.1. Rate-determining steps of reactions. For solid-state fluorination to occur, relatively more volatile fluorinated fullerenes should be removed from the reaction mixture to the gas phase, due to which they cannot accumulate in the reaction zone. Removal of these fullerenes is evidenced by the average surface concentrations of fluorofullerenes in the reaction zone, which are represented by the activities of the components of the reaction mixture (Table 3). The activities are formally calculated by normalizing the measured partial pressures to the corresponding saturated vapor pressures. These calculations were carried out only for the $C_{60}F_{18}$ and $C_{60}F_{36}$ products using known data on the vapor tension.[26] The activities of fluorinated fullerenes are several orders of magnitude smaller than unity and, consequently, their surface concentrations are low compared to the concentration of the molecules on the surface of pure fluorofullerene crystals. Since the densities of solid fluorofullerenes are comparable with that of fullerite, it can be concluded that the fullerite surface in the reaction mixture is weakly occupied by fluorofullerene molecules.

In systems, where fullerene is initially present in an excess amount (for example, in the C_{60}/Na_3PbF_7 reaction), the activity of C_{60} is close to unity in all reaction steps, including the initial step. In other words, fullerene vaporization under the conditions of a reaction mixture, occurs analogously to that of the pure compound. In the presence of excess SFA (the C_{60}—K_3PbF_7 system), the activity of C_{60} is substantially lower than unity already in the initial reaction steps, the activities of fluorinated products remaining low.

Table 3. Activities of fluorofullerenes and overall flows of fluorinated products from an effusion cell in the C_{60}/Na_3PbF_7 reactions

t/min	T/K	$a(C_{60})^a$	$a(C_{60}F_{18})$	$a(C_{60}F_{36})$	$\nu_{prod}{}^b/s^{-1}$
			Na_3PbF_7		
195	643	0.68	—	$3.56 \cdot 10^{-3}$	$5.60 \cdot 10^{14}$
235	643	0.28	—	$2.58 \cdot 10^{-3}$	$4.11 \cdot 10^{14}$
805	653	0.71	—	$1.43 \cdot 10^{-3}$	$3.46 \cdot 10^{14}$
864	648	0.55	$4.55 \cdot 10^{-3}$	$6.32 \cdot 10^{-4}$	$1.21 \cdot 10^{14}$
889	648	0.51	$4.09 \cdot 10^{-3}$	$5.26 \cdot 10^{-4}$	$1.16 \cdot 10^{14}$
1104	686	0.97	$1.54 \cdot 10^{-2}$	$6.55 \cdot 10^{-5}$	$2.04 \cdot 10^{14}$
			K_3PbF_7		
540	620	0.344	—	$1.53 \cdot 10^{-2}$	$5.48 \cdot 10^{14}$
595	637	0.079	—	$3.00 \cdot 10^{-3}$	$2.13 \cdot 10^{14}$
1271	699	0.020	$2.41 \cdot 10^{-4}$	$6.30 \cdot 10^{-5}$	$4.73 \cdot 10^{13}$
1346	699	0.017	$1.28 \cdot 10^{-4}$	$2.38 \cdot 10^{-5}$	$1.83 \cdot 10^{13}$
1490	711	0.003	$8.41 \cdot 10^{-6}$	$4.68 \cdot 10^{-7}$	$6.87 \cdot 10^{11}$

[a] Calculated as $a(i) = P(i)/P°(i)$, where i is the number of fluorine atoms in $C_{60}F_i$ molecules.

[b] The absolute value of the molecular product flow through an effusion orifice: $\nu_{prod} = \Sigma\nu(C_{60}F_i) - \nu(C_{60})$.

In both cases, we observed virtually equal overall fluorination rates, all other factors being the same. In our experiments, these rates were monitored by measuring the overall product flow from an effusion cell. For example, using the data given in Table 3 and taking into account the ratios of the total reaction surface area to the effusion surface,[19] the overall molecular flow (including evaporation of C_{60}) from the unit surface area in the C_{60}—Na_3PbF_7 system (a deficient amount of SFA) was evaluated to be $1.1 \cdot 10^{16}$ m^{-2} s^{-1}. This value was determined from the partial pressures of all reaction products, which were measured at 643 K within 235 min after the beginning of the reaction. In the C_{60}—K_3PbF_7 system (excess SFA), the corresponding value (T = 637 K and t = 595 min, respectively) is $1.2 \cdot 10^{16}$ m^{-2} s^{-1}.

Under the conditions of a constant inlet flow of fluorine, the C_{60}/F_2 reactions in the presence of chemically active matrices also retain the overall fluorination rate, while the composition of the products sharply changes.[21]

Below we propose an explanation for the above-described experimental facts. At not too low temperatures, the rate of *topochemical reactions* is often limited by reagent diffusion to the reaction zone. In reactions between two solid reagents, there are two contradirectional diffusion flows: (1) the active fluorine flow and (2) the fullerene flow. The C_{60} crystals belong to the so-called plastic crystals characterized by high imperfection. When considering fullerene diffusion to the reaction zone, one should consider the flow of defects to the crystal surface, which is in mechanical contact with SFA or its decomposition products.

In the C_{60}/Na_3PbF_7 and C_{60}/K_3PbF_7 reactions, different macroscopic steps are, apparently, the rate-determining steps depending on whether the reaction mixture contains an excess or deficient amount of SFA. If the reaction mixture contains an excess of SFA in the absence of deficiency of fluorine, the fluorine concentration in the reaction zone remains high throughout the reaction. This is favorable for the formation of highly fluorinated products, and the fullerene flow to the reaction zone is a rate-determining step. In the presence of excess fullerite, the initial reaction step also affords highly fluorinated products, which are changed for lowly fluorinated products as fluorine becomes deficient. Since the latter products are substantially less volatile, they can be detected only at higher temperatures. If fullerite is present in an excess amount, its activity remains equal to unity throughout the experiment. In the presence of excess SFA, the activity of fullerite decreases from the very beginning of the reaction and finally decreases by several orders of magnitude. Since the activity of fluorofullerenes is low, a decrease in activity of fullerite can be explained only by the fact that C_{60} molecules that are evaporated react with the SFA surface.

In reactions proceeding in the presence of chemically active matrices, fullerene diffusion to the reaction zone is always a rate-determining step, because an excess of fluorine is provided by its rather extensive flow from the outside. Experimental data demonstrate that the activity of C_{60} can decrease even more substantially and lead to the complete disappearance of the $C_{60}{}^{+}$ ion from the EI mass spectrum of the gas phase.

7.2. Changes in the composition of the products during the reaction. Experimental data on solid-state fluorination provide evidence that the reaction is accompanied by a gradual shift to less fluorinated fullerenes, which displace the major product in the final step. This phenomenon is observed in all reactions with excess C_{60}. As an example, the mass spectra, which were successively measured during the reaction with CoF_3 (where this effect is most pronounced), are shown in Fig. 7. It can be seen that rapid redistribution of the reaction products occurs in a particular reaction step, which makes it possible to selectively prepare $C_{60}F_{18}$. This compound is generally synthesized with the use of a much stronger SFA, K_2PtF_6.

If the reaction is performed under isothermic conditions, the parameter ξ is the only variable in Eqs (9) describing the successive partial pressure ratios of the products. An increase in the parameter ξ during the reaction occurs due to a decrease in the fluorine concentration C_F as a result of gradual accumulation of decomposition products of SFA in the reaction zone. The influence of this factor on the composition of the products is demonstrated in Fig. 6. Under real conditions, a change in the composition is not smooth, because a slow change in the parameter ξ is combined with the factor associated with the jumps in the activation energies. As a results, the observed dynamics of distribution of gaseous products can be described as a rapid transformation from highly fluorinated to low fluorinated fullerene, avoiding products from $C_{60}F_{18}$ to $C_{60}F_{36}$ (see Fig. 7).

From the kinetic model, it follows that, at constant temperature, a linear correlation between the ratios of the rate constants of fluorine addition is held for each three successive products, $C_{60}F_n$, $C_{60}F_m$, and $C_{60}F_k$:

$$a(k_n/k_m) + k_k/k_m = b. \qquad (15)$$

Experimental data on the relative instantaneous formation rates of fluorofullerenes by solid-state fluorination, which were determined from their partial pressures, confirmed that the linear dependence (15) is actually fulfilled, and it was demonstrated how this dependence can be used to experimentally determine the differences between two successive activation energies.[19,24]

In the cited studies, using the reaction with MnF_3 as an example, the rapid change to another major product in solid-state fluorination was shown to be adequately described in a quantitative way in terms of the proposed model. It appeared that the relative change in the formation rate of the $C_{60}F_{18}$ and $C_{60}F_{36}$ products by more than two orders of magnitude can occur in the case of a *smooth* increase in ξ_{36} by only a factor of five. In this case, local selectivity within three $C_{60}F_{34}$, $C_{60}F_{36}$, and $C_{60}F_{38}$ compounds is not violated. Simple estimates show that a loss of selectivity occurs if the parameter ξ_{36} increases much more substantially (by a factor of 30—40), which is possible only if the concentration C_F decreases proportionally, *i.e.*, in the case of a sharp decrease in the overall reaction rate. Therefore, the relative yields of compositionally similar products are determined by the difference

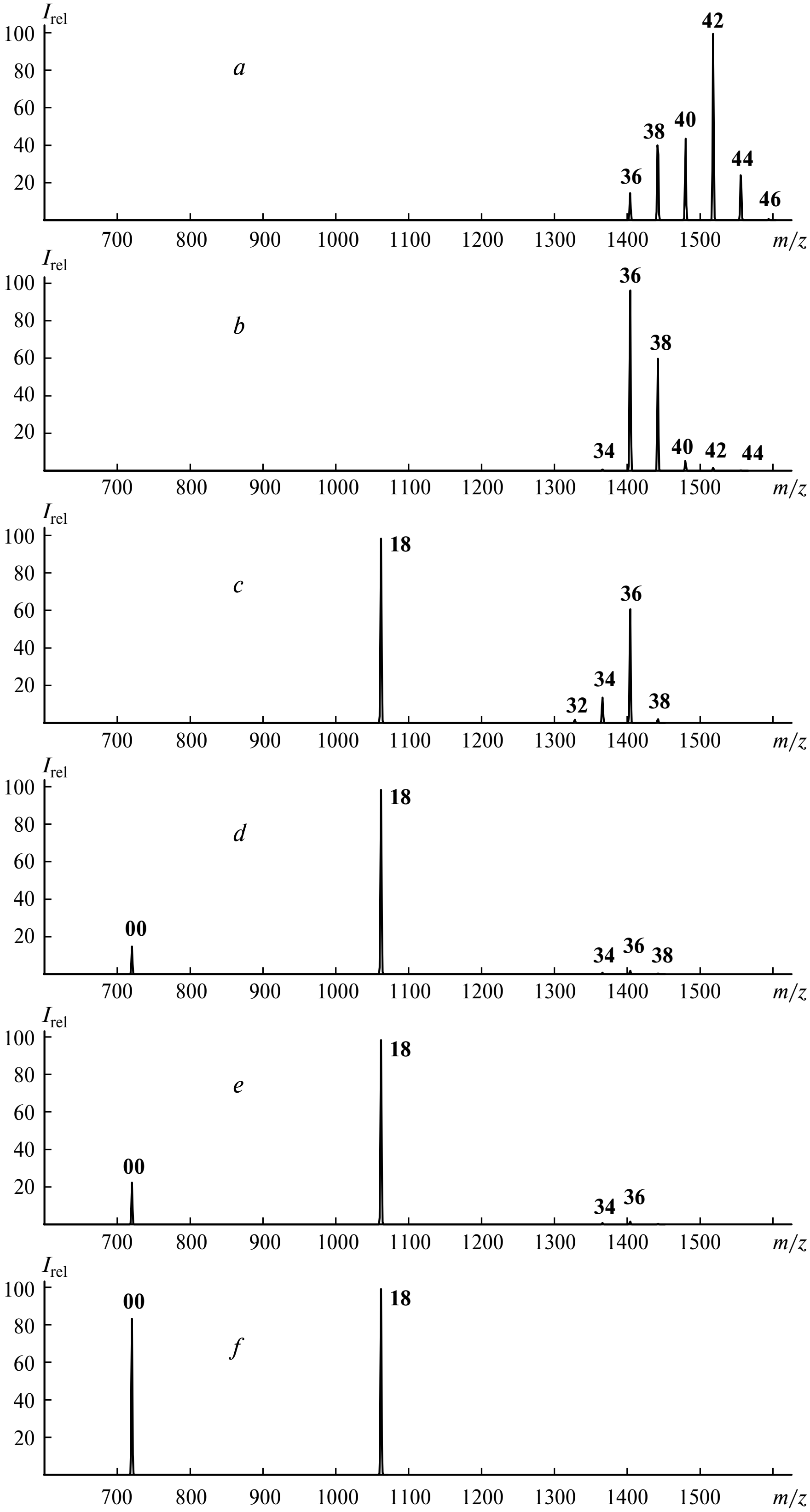


Fig. 7. Changes in the composition of products with time for the reaction of C_{60} with cobalt trifluoride; the time intervals from the onset of the reaction are given: *a*, 653 K, 700 min; *b*, 653 K, 830 min; *c*, 697 K, 1100 min; *d*, 702 K, 1120 min; *e*, 705 K, 1135 min; *f*, 704 K, 1185 min.

in the activation energy between the successive reactions of addition of F to $C_{60}F_{34}$ and $C_{60}F_{36}$. This difference is about 50 kJ mol^{-1} for the C_{60}—MnF_3 reaction system. This parameter can be controlled only by varying SFA. For compositionally different products, such as $C_{60}F_{18}$ and $C_{60}F_{36}$, large relative changes in the yields can be achieved by varying the fluorine concentration even if the activation energies are equal. This follows from the theory and was confirmed by experimental data. Therefore, the compositions of the products can be varied by controlling the concentration C_F.

However, an essential drawback of solid-state fluorination is that the concentration of active fluorine and, consequently, the fluorination rate at given reagent dispersity and density depend only on the temperature, and this makes it difficult to vary C_F within the required limits. The use of a F_2 flow in the presence of chemically active matrices offers an advantage, because the temperature and fluorine flow can be varied independently, thus providing additional possibilities to control the yields of the products. For example, an increase in the temperature at a given flow level makes it possible to virtually completely terminate the reaction at the step of formation of $C_{60}F_{18}$. The use can be made of a sharp increase in the distillation rate of this product to the gas phase, which hinders a further increase in the degree of fluorination. An increase in the fluorine flow at this new temperature can resume the formation of higher fluorinated products.

All concepts of the SSF model are applicable to the C_{60}(solid)/F_2(gas) reactions in the presence of chemically active matrices because the mode of fluorine transfer to fullerite in the presence of chemically active matrices is similar to that in solid-state fluorination. In Fig. 8, the time dependences of the EI mass spectra of gaseous products, which were obtained with the use of a MnF_2 matrix at constant temperature and a steady-state fluorine flow (*a—e*) and in the C_{60}/MnF_3 reaction (*f—j*), are given for comparison. It can be seen that the reaction in the matrix proceeds through the steps identical to those involved in the analogous SSF but in the reverse order. This is attributable to a gradual increase in the surface concentration of adsorbed (active) fluorine, resulting in a decrease in the parameters ξ. In turn, C_F increases due to a fluorine flow from the outside, which is excessive compared to the diffusion flow of C_{60} to the reaction zone. The concentration C_F can be decreased by controlling the fluorine flow, thus again obtaining low-fluorinated products. By contrast, late reaction steps of solid-state fluorination are always accompanied by depletion of the solid reagent mixture in fluorine. Hence, the use of chemically active matrices offers additional possibilities of searching for the reaction conditions with the aim of preparing the desired products even without changing the matrix.

We described the above phenomenon with the use of only the *relative* formation rates of the major products in the gas phase. For the practical synthesis of fluorofullerenes, in which the amount of the product is also of importance, the corresponding *absolute* rates are of significance. Here, one can use the temperature dependences of the absolute rate constants of fluorination and the saturated vapor tensions of fluorofullerenes, which, unlike the dependence of the relative rate constants, are sufficiently *strong* (characteristic activation and sublimation energies are 120—180 kJ mol^{-1}). Due to a large difference in the vapor tensions of $C_{60}F_{18}$ and $C_{60}F_{36}$, one or another of the reaction products is removed from the reaction by sublimation at substantially different temperatures. An extensive escape of one compound to the gas phase can be provided by changing the temperature and thus virtually terminate the reaction as soon as the desired product is formed.

7.3. Activation energies in reactions with the use of various matrices. The activation energies of fluorination vary with changes in the nature of SFA or chemically active matrices. There is a general tendency for an increase in the activation energy in reactions with the use of weaker agents. However, the activation energies in different steps of addition of fluorine to fullerene increase to a different degree. According to the BEP principles, the largest increase should be observed in the step (see Scheme 4), where the enthalpy is closest to zero, which can give rise to a slow step with an activation energy sufficiently high for the selective formation of the corresponding product.

Let us consider the results of the kinetic study of SSF from this point of view. The numerical values of the activation energy jumps (see Table 2) clearly show the relationship between the differences in E_a and the chemical nature of SFA. For the solid fluorinating agents MnF_3 and CoF_3, this relationship is most obvious, because their relative arrangement on the fluorinating ability scale is known. The latter compound is a stronger fluorinating agent than the former compound, which is reflected in the ~20 kJ mol^{-1} difference between the activation energies for the same pair of reactions

$$C_{60}F_{34} + 2\,F = C_{60}F_{36},$$

$$C_{60}F_{36} + 2\,F = C_{60}F_{38}.$$

The replacement of MnF_3 with CoF_3 leads to a negative shift of this difference, which signifies that a decrease in the absolute value of E_a for the latter reaction was larger than that for the former one.

Two families of similar reactions are exemplified by two pairs of the reactions (6) ($C_{60}F_{34}$ and $C_{60}F_{36}$ as the starting reagents): (1) the reaction involving MnF_3 and (2) the reaction involving CoF_3. The families are

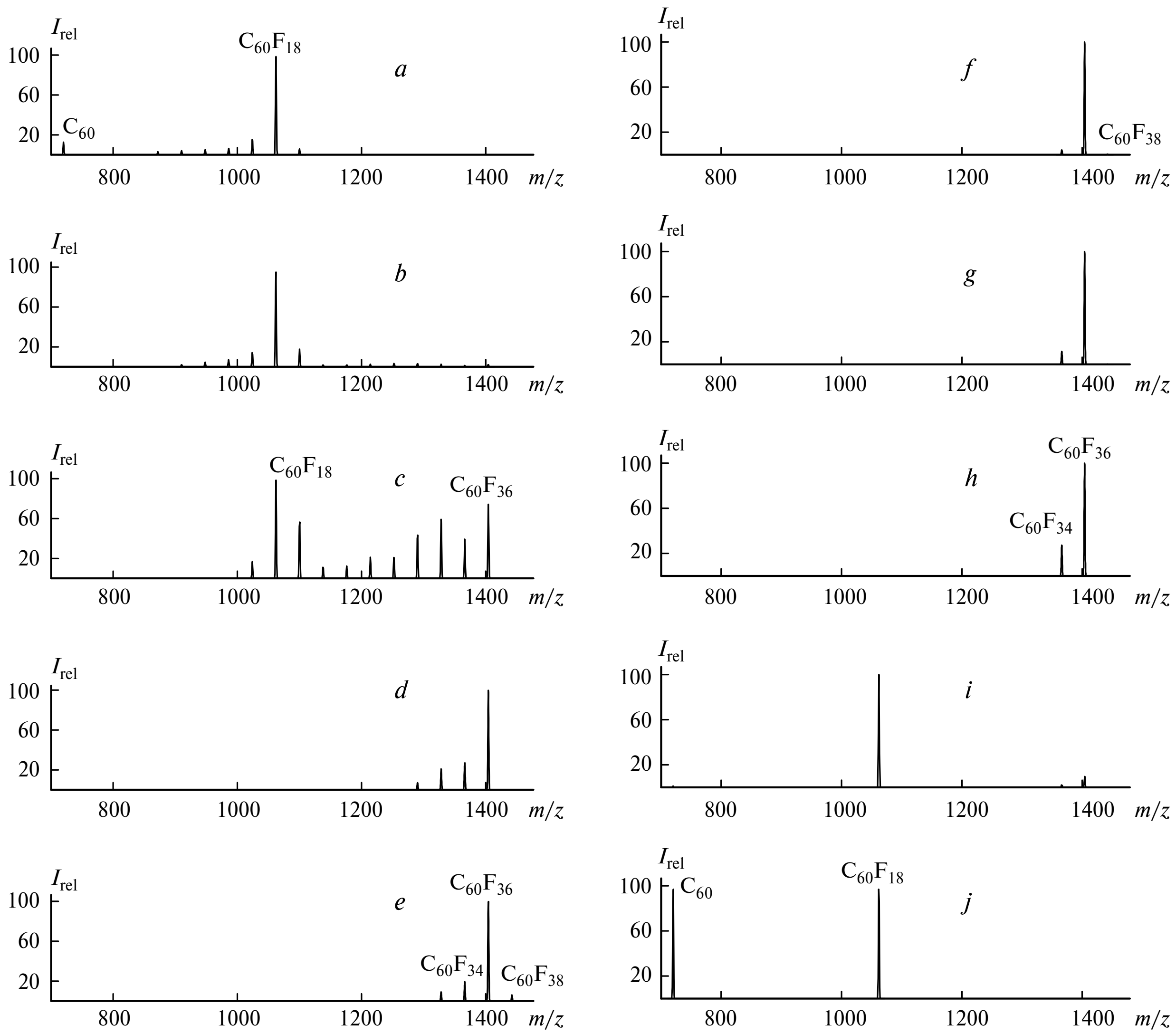


Fig. 8. Comparison of an evolution with time of the distribution of products prepared by fluorination of C_{60} with elemental fluorine in the presence of a chemically active matrix (*a—e*) and by solid-state fluorination (*f—j*):

	T/K	t/h		T/K	t/h		T/K	t/min		T/K	t/min
a	720	4.4	*d*	720	11.7	*f*	626	620	*h*	663	1115
b	720	8.0	*e*	720	14.9	*g*	626	845	*i*	663	1145
c	720	10.2							*j*	663	1315

denoted by the Roman numerals I and II, respectively, and the reactions are indicated by the Arabic indices 1 and 2, respectively. Then, using Eq. (7), we can write the following equations for the jumps within each family

$$\delta E_{\mathrm{I}} = B_{\mathrm{I}}(\Delta H_2 - \Delta H_1), \qquad \delta E_{\mathrm{II}} = B_{\mathrm{II}}(\Delta H_2 - \Delta H_1). \tag{16}$$

The values $\Delta H \equiv \Delta H(6)$ include the enthalpies of abstraction of the fluorine atom from the SFA surface (ΔH_{MF}) and the enthalpies of addition of the fluorine atom to the carbon cage ($\Delta H_{\mathrm{CF}} \approx D_{\mathrm{CF}}$): $\Delta H = \Delta \mathrm{H}_{\mathrm{MF}} - D_{\mathrm{CF}}$. In each family (in the presence of the same SFA), this parameter is a function of only D_{CF}, so that

$$\delta E_{\mathrm{I}} = -B_{\mathrm{I}}(D_{\mathrm{CF(2)}} - D_{\mathrm{CF(1)}}),$$

$$\delta E_{\mathrm{II}} = -B_{\mathrm{II}}(D_{\mathrm{CF(2)}} - D_{\mathrm{CF(1)}}). \tag{17}$$

Based on the results of combustion calorimetry, it can be stated that $D_{\mathrm{CF(2)}} < D_{\mathrm{CF(1)}}$. Hence, the differences in the parentheses are negative. The difference between the jumps gives:

$$\delta E_{\mathrm{I}} - \delta E_{\mathrm{II}} = (D_{\mathrm{CF(2)}} - D_{\mathrm{CF(1)}})(B_{\mathrm{II}} - B_{\mathrm{I}}). \tag{18}$$

Hence, if $B_{II} < B_I$, this difference has the required positive value observed in experiments. The latter inequality is valid in terms of the BEP approach, if the elementary reactions of both $C_{60}F_{34}$ and $C_{60}F_{36}$ with CoF_3 are more exothermic than the analogous reactions with MnF_3. This, in turn, indicates that the enthalpy of abstraction of the fluorine atom from the SFA surface is smaller for CoF_3 than for MnF_3, as it must for a stronger SFA.

Hence it follows that the BEP principles are applicable to the solid-state reactions under consideration. A comparison of the reactions of C_{60} with MnF_3 and CoF_3 provides a good example of how a decrease in the difference in the activation energies for two reactions with the use of a stronger SFA (CoF_3) leads to a loss of selectivity to $C_{60}F_{36}$ (see Fig. 7). This is also evident from the composition of the resulting condensate,[19] in which $C_{60}F_{42}$ was present as the major compound combined with a substantial fraction of compositionally similar compounds.

The opposite effect associated with a decrease in the exothermic effect of the reaction is observed, for example, on going from MnF_3 to $BaPbF_6$. Both reactions afford $C_{60}F_{36}$ as the major product. However, selectivity of the reaction with a complex salt is much higher. The use of this complex fluoride provided very high (higher than 98%) selectivity to $C_{60}F_{36}$. Evidently, $BaPbF_6$ is a weaker fluorinating agent than MnF_3, due to which the enthalpy of the elementary fluorine exchange reaction approaches zero. Correspondingly, the difference in the activation energy $E_{36} - E_{34}$ increases approximately from 50 to 70 kJ mol^{-1}. Unfortunately, the lack of reliable thermodynamic data on complex fluorides makes it impossible to construct a quantitative dependences of the difference in the activation energy on the fluorinating ability of SFA.

The diagram presented in Fig. 9 can serve as a qualitative illustration of the correlation between the thermodynamic and kinetic energy parameters. It can be seen that a large negative jump in the C—F bond energy in a fluorofullerene molecule is always accompanied by a substantial positive jump in the corresponding activation energy. In the interval between the $C_{60}F_{18}$ and $C_{60}F_{36}$ compounds, where the energy D_{CF} changes more smoothly, the activation energies also vary only slightly. The same is true for the $C_{60}F_{n>36}$ products. From analogous considerations, the negative jump in the C—F bond energy can be predicted between $C_{60}F_{18}$ and $C_{60}F_{20}$, for which an estimate is lacking. According to the kinetic data, this jump should be smaller than that between $C_{60}F_{36}$ and $C_{60}F_{38}$.

The results given in Table 2 demonstrate that, due to small differences in the activation energies of the attachment of F atoms to molecules stoichiometrically different from $C_{60}F_{18}$ and $C_{60}F_{36}$, the steps giving rise to these compounds appear to be equally fast. Hence it follows that the fine tuning of solid fluorinating agents for the selective synthesis of the intermediate $C_{60}F_n$ compounds (n = 20—34) is a complicated problem. However, it is easy to provide a high percentage of the desired compounds in the sample synthesized and prepare mixtures, in which their concentrations are sufficient for chromatographic isolation as individual compounds, by independently varying (with the use of a matrix) the fluorine pressure and temperature.

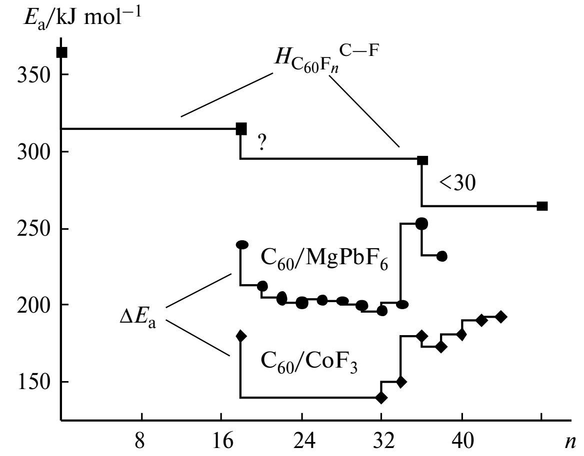


Fig. 9. Activation energies of different fluorination steps of C_{60} with SFA and the enthalpies of C—F bond cleavage in fluorofullerene molecules: n is the number of F atoms in the molecule, $H_{C_{60}F_n}{}^{C-F}$ are the enthalpies of C—F bond cleavage in $C_{60}F_n$ molecules.

The results of the reaction with CoF_3 giving rise to a large percentage of products with a high (compared to $C_{60}F_{36}$) fluorine content can be supplemented by the results of the reactions with $MgPbF_6$ and MnF_3, which give all fluorofullerenes in a range from $C_{60}F_{18}$ to $C_{60}F_{36}$ when performed over a rather long period of time (~2 and 3 h, respectively). The percentage of each product estimated from the partial pressures in the gas phase is 5—10%. Therefore, the starting compound for the preparation of individual fluorine derivatives in a range from $C_{60}F_{18}$ to virtually $C_{60}F_{48}$ can be synthesized using the available matrices of low-valent metal fluorides produced by removing fluorine from SFA.

8. Isomers of fluorine derivatives of C_{60} in solid-state fluorination

Due to a wide variety of the arrangement modes of fluorine atoms at the carbon cage in fluorofullerene molecules, numerous isomers of these compounds can occur, although only a few of them are generated by solid-state fluorination. A series of isomers were isolated for some compounds synthesized in a stoichiometrically pure form. For example, only one isomer with the C_{3v} symmetry, was identified and structurally characterized for $C_{60}F_{18}$,[28] which was prepared by the reaction with K_2PtF_6.[13] In this isomer, all 18 fluorine atoms are bound to one hemisphere of the cage. For $C_{60}F_{36}$, two most abundant isomers[29,30] with the C_3 and T symmetry, which are formed simultaneously in the reactions with MnF_3,[11] were detected. Fluorination of C_{60} with molecular fluorine also affords two structurally similar isomers of $C_{60}F_{48}$, one of which (its percentage in the mixture is higher) occurs as an enantiomeric pair with the D_3 symmetry, and another isomer is an achiral form with the S_6 symmetry.[31]

The results of the study[32] cast doubt on the hypothesis of the successive addition of fluorine atoms in solid-state fluorination giving fluorinated fullerenes. The $C_{60}F_{20}$ compound was chromatographically isolated from the condensate accumulated after the reaction of C_{60} with potassium hexafluoroplatinate diluted with KF. X-ray diffraction study of $C_{60}F_{20}$ revealed a very unusual equatorial arrangement of the fluorine atoms at the carbon cage. Evidently, the molecule with this structure cannot be prepared by the direct addition of two F atoms to the $C_{60}F_{18}$ molecule having the above-described geometry.

This contradiction can easily be accounted for by the data, according to which the rate of solid-state fluorination corresponds to the flow density of active fluorine to the reaction zone of about 10^{15}—10^{17} atom s^{-1} m^{-2} (see Table 1). Taking into account the surface molecular density of C_{60} crystals (~10^{17} m^{-2}), this indicates that the fullerene molecule binds, on the average, one fluorine atom per second. Even with the need to consider only a small portion of surface-active molecules as reacting with fluorine, the lifetime between two events of the fluorine attack is much longer than the characteristic time of any intramolecular motion. Hence, the fluorofullerene molecule has time to adopt a structure corresponding to a thermodynamically stable isomer.

The authors of the study[33] reasoned that the geometric structures of $C_{60}F_{18}$ and the most abundant isomer of $C_{60}F_{36}$ with the C_3 symmetry are incompatible with both forms of $C_{60}F_{48}$, because the latter cannot be generated by the simple addition of pairs of fluorine atoms at free double bonds. Nevertheless, experiments demonstrated that the $C_{60}F_{48}$ product with an identical isomeric composition was prepared by the reaction with F_2 regardless of whether C_{60}, $C_{60}F_{36}$, or even a $C_{60}F_{16}$—$C_{60}F_{42}$ mixture is used as the starting reagent. This result can be explained only on the assumption of easy intramolecular migration of fluorine atoms during the reaction.

It is not inconceivable that, due to a favorable combination of the activation energies in the reactions with the use of particular new solid fluorinating agents, the addition of fluorine in a certain step can follow a pathway different from that giving rise to the already known isomers of fluorofullerenes. Nevertheless, the proposed kinetic model ignores the difference between isomers, although the corresponding changes can be easily introduced if required. In this case, the reaction sequence (see Scheme 4) will involve competitive reactions responsible for different pathways of addition of fluorine atoms. However, it is unlikely that this modification is of practical importance nowadays taking into account the lack of adequate data on isomers and a wide variety of possible new pathways. In any case, it is necessary to preliminarily select the most stable isomers using calculation methods. Experimentally, mass-spectrometric detection of gaseous reactions products should be supplemented with analysis of the condensate with consideration for taking into account the isomeric composition. Analysis should be performed at different instants of time during the reaction, *i.e.*, the reaction should be interrupted to withdraw samples of the condensate.

9. Conclusion

The above-considered theoretical concepts and experimental procedures, which were developed for the determination of the kinetic parameters of the reactions based on these theoretical concepts, can be extended to solid-state fluorination of C_{70} and higher fullerenes. Studies devoted to the synthesis of fluorine derivatives were carried out independently, although primarily *in situ*, and were limited by the fact that the starting reagents are less readily available.[2,11] It was found[2,11] that the reactions with C_{60} most easily produce $C_{60}F_{36}$ and $C_{60}F_{18}$, whereas C_{70}, C_{76}, and C_{84} give compounds with the magic number of fluorine atoms having the formulas $C_{70}F_{38}$, $C_{76}F_{26}$, and $C_{84}F_{40}$, respectively. The degree of selectivity, which can be achieved for higher fullerenes, is substantially lower than that with respect to $C_{60}F_{36}$. Apparently, the differences in the C—F bond energies of higher fullerenes are less pronounced than those of C_{60}.

All the aforesaid is also true for endohedral fullerene derivatives, because the presence of atoms or even chemical groups within the closed carbon cage should not lead to a change in the reaction mechanism of exopolyaddition, although it can exert an effect on the reactivity. Recent investigations[34,35] have demonstrated that the structures of the most stable isomers of endohedral fullerenes can differ from those of the corresponding molecules with an empty cage. This should be reflected in the character of the resulting derivatives. Pioneering studies on solid-state fluorination of endohedral metal derivatives of C_{60} are presently underway.

As for fullerene derivatives with other small functional groups, it should be noted that solid-state reactions, analogous to solid-state fluorination, cannot be used for the synthesis of chloro- or bromofullerenes because of low thermal stability of these compounds. We failed to bind CN groups to C_{60} in the solid state through the reactions with complex cyanides containing, as in the case of fluorides, variable-valence metals. This is associated with the fact that heating leads to the predominant transfer of these groups to the gas phase in the dicyane form. Finally, studies on the synthesis of trifluoromethylated fullerenes $C_{60}(CF_3)_k$ according to a procedure analogous to SSF are presently underway, CF_3COOAg being used as a source of CF_3 groups.[36,37] Mass-spectrometric analysis provided evidence for the formation of derivatives with the number of group in a range of k = 2—20. Apparently, a high degree of functionalization indicates that these reactions not only superficially resemble SSF (solid reagents are mixed) but also proceed by a similar mechanism associated with the successive addition of the functional groups in the solid state. However, this problem remains to be explored. Therefore, the reactions between solid compounds analogous to SSF were carried out only with fluorides.

A different situation arises with the reactions in solution, which are often used to prepare chlorine and bromine derivatives of fullerene. An analogy with solid-state reactions will be observed if a particular step of the addition reaction could be substantially slowed down by choosing appropriate reagents and if one will succeed in sharply increasing the rate of removal of the corresponding product from the reaction zone through precipitation from the solution upon complexation or crystallization. This, in principle, can be achieved by decreasing solubility as a result of a change in the temperature or a choice of an appropriate solvent.

The main conclusions can be briefly summarized as follows. Fluorination of fullerene allows one to find a slow step in the sequence of successive addition reactions and selectively prepare the desired product using even a small change (~20 kJ mol^{-1}) in the energy of the C—F bond cleavage on going from $C_{60}F_{2m}$ to $C_{60}F_{2m+2}$. This is achieved by decreasing the exothermic effect of the reactions with the use of softer fluorinating agents. An appropriate agent can be chosen based on the Evans—Polanyi principle, according to which the activation energies depend linearly on the enthalpies of the corresponding elementary steps. Additional possibilities for performing selective reactions are associated with the control over the rate of removal of volatile products from the reaction mixture.

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