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Theoretical Study of Isomerization Mechanisms in Fluorinated Fullerene Derivatives

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Various candidate processes that can effect rearrangement of the shell of addends are being discussed for $C_{60}F_x$ and $C_{60}(CF_3)_y$ compounds. It is shown that isomerization of fluorofullerenes is catalyzed by other fullerene molecules or organic donors, while in trifluoromethylated fullerenes such catalysis is inefficient. These observations afford an explanation for important differences between fluorides and CF_3 derivatives of C_{60} in distribution of products of their high-temperature syntheses.

Introduction

Low volatility and high thermal stability of fullerenes make possible their high-temperature polyfunctionalization with fluorine atoms and fluorocarbon groups such as CF_3 via rather simply organized reactions with fluorine gas,[1,2] transition metal fluorides,[3,4] silver trifluoroacetate,[5,6] and trifluoromethyl iodide.[7,8] Apart from being convenient model systems for studying regiochemistry of sequential polyaddition to fullerenes, $C_{60}F_x$ and $C_{60}(CF_3)_y$ molecules also demonstrate enhanced electron acceptor properties as compared to pristine carbon cages and thus may be of potential interest for photovoltaic applications.[9,10] Both families of compounds have their own merits: higher fullerene fluorides show very remarkable electron affinity values[11,12] but can be prone to hydrolysis,[13] while trifluoromethylated fullerenes show less pronounced electron-withdrawing properties[14] but bear inert addends.

The most intriguing difference between fluorinated and CF_3 derivatives of fullerenes is the ranges of available synthetic products. Among the $C_{60}F_x$ compounds only those with x = 18,[2] 36,[3] and 48[1] can be readily prepared as major products, x = 2−8,[15,16] 16,[17,18] 20,[19] and 38[20] being additionally available via chromatographic isolation and $C_{60}F_{24}$ via a very different low-temperature substitutional protocol.[21] Furthermore, for each of the above compounds only very few most stable isomers from an enormous number of theoretically possible structures can be obtained, thus suggesting thermodynamic control during their formation. Indeed, it has been shown that fluorination of both C_{60} and $C_{60}F_{36}$ leads to the same most stable isomers of $C_{60}F_{48}$, which do not incorporate a substructure of $C_{60}F_{36}$.[22] In other words, there takes place high-temperature rearrangement of the shell of fluorine addends termed in ref 22 as “fluorine dance”. Moreover, there has been reported slow room temperature interconversion of C_1 and C_3 isomers of $C_{60}F_{36}$ in solution in the presence of ambient atmosphere,[23] suggesting possible nucleophilic effects of moisture.

$C_{60}(CF_3)_y$ compounds show a somewhat different picture. Although their available isomers analogously find themselves among the most energetically stable structures,[24–26] the number of these available isomers is much greater and their stability ranges are broader.[24–26] At the same time, some highly stable isomers may be missed in the synthesis.[24] Therefore, even though there exist some indications of the possibility of CF_3 migration in trifluoromethylated fullerenes, it is likely that such migration is more hindered than in fullerene fluorides, which precludes attainment of complete equilibration for the isomers with the same degree of addition.

Easier transformations of fluorinated fullerenes may seem somewhat surprising, as one could expect $C-CF_3$ bonds to be generally weaker than $C-F$ bonds. Despite fluorine being bound to C_{60} somewhat more weakly, though not critically, than in common organic compounds[27] and similar observations for fullerene hydrides[28] and chlorides[29] suggesting this to be a common phenomenon for $C_{60}-X$ bonds, high thermal stability of trifluoromethylated and fluorinated fullerenes demonstrates that $C_{60}-F$ and $C_{60}-CF_3$ bonds remain remarkably strong. However, sigmatropic shifts of fluorine atoms are known for smaller unsaturated organic molecules. In particular, they were found to take place in the course of pyrolysis of fluorinated cyclohexadienes.[30] Later, it has been shown that equilibrium in such systems is reached much faster in the presence of F^- anions.[31] From a general point of view, one has to consider various possibilities of catalysis of addends migration by some external molecule or particle rather than the simple repetitive acts of the consecutive breaking of an existing bond and formation of a new one.

In the present theoretical study, we compare two possible instances of addends migration in $C_{60}F_x$ and $C_{60}(CF_3)_y$: intramolecular shift of an addend between the adjacent free sites and intermolecular exchange between the neighboring fullerene molecules, which can be the case in the solid phase mixtures under the conditions of the above-mentioned high-temperature syntheses. Besides, we consider the negative charging-, nucleophile-, and electron donor-induced solution phase isomerization of $C_{60}F_{36}$ as an example of possible reactions that utilize high electron affinity of higher fluorofullerene molecules.

Computational Methods

The computations of stationary and transition states, as well as reaction paths, have been carried out at the DFT level of

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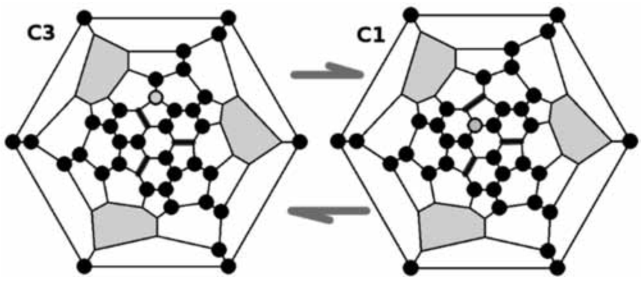

Figure 1. Scheme of allylic 1,3-shift that couples C_1 and C_3 isomers of $C_{60}F_{36}$. The migrating fluorine atom is denoted by an empty circle.

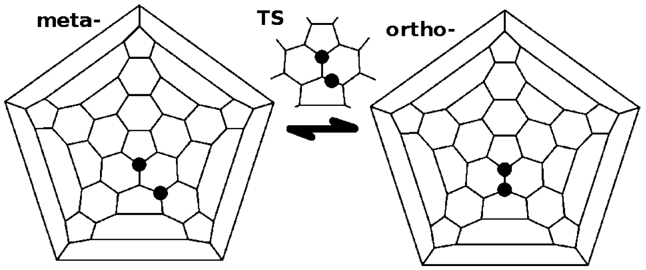

Figure 2. Schlegel diagram representation of the meta−ortho transformation of $C_{60}F_2$. TS denotes transition state.

theory with the use of the PRIRODA package[32] that employs an efficient implementation of the resolution-of-the-identity (RI) approach. PBE exchange-correlation GGA-type functional[33] and a built-in TZ2P basis set (TZP for hydrogen atoms) were used. This approach has been widely tested in our group to provide good description of various molecular properties of fullerenes such as geometric parameters, electron affinity, etc. Notwithstanding its general deficiencies when applied to processes that involve bond breaking, DFT seems the most adequate approach to the reactions of fullerenes where the electronic properties are determined by the whole carbon shell rather than its local fragments, thus requiring treatment of the whole molecule on the same level.

Preliminary geometry optimizations for further DFT refinement have been carried out at the AM1 level of theory with the use of the PC-GAMESS/Firefly package[34] partially based on the GAMESS-US source code.[35]

Results and Discussion

1. Fluorinated Fullerenes.

a. Intramolecular Shifts of Fluorine Atoms. The first question that arises when studying migration of an addend over a fullerene cage is whether the said migration is easier to proceed stepwise via hopping between adjacent atoms or via more distant jumps. A survey of several model systems clearly suggests that for a fluorine atom migration between the adjacent sites, i.e., 1,2-shift (or sequences thereof), is usually preferable over more remote relocations. To illustrate this, we considered allylic 1,3-shift of a fluorine atom that couples almost isoenergetic C_1 and C_3 isomers of $C_{60}F_{36}$ as schematically shown in Figure 1. Although, as was mentioned above, these two isomers can be in slow exchange in solution due to some effects of ambient atmosphere,[21] scanning of the potential energy surface of an isolated molecule with respect to position of the migrating fluorine atom yielded no transition states more energetically favorable than complete dissociation of the respective C−F bond. Thus, the activation energy of 1,3-shift of a fluorine atom between the two stable structures was found to exceed 300 kJ/mol, meaning that such a rearrangement channel may play any role only at very high temperatures concurrently with decomposition. No more favorable is the corresponding sequence of two 1,2-shifts, as intermediate structure is a highly unstable biradical.

As an example of easier proceeding 1,2-shifts, one can consider transformation of meta-$C_{60}F_2$ into ortho-$C_{60}F_2$, as sketched in Figure 2. The activation barriers for this process may serve as sort of a limiting estimate for the whole class of 1,2-shifts since the said two isomers exhibit a drastic difference in formation energy—178 kJ/mol in favor of the para-structure. As a result, meta-to para-fluorine atom shift is characterized by a barrier of only 56 kJ/mol. Thus intramolecular migration of fluorine in fluorofullerenes may take place in the case of transient formation of highly relatively unfavorable structures. Such isomers will rapidly rearrange, provided they have a much more favorable alternative that can be reached via a 1,2-shift of fluorine atom. However, even 1,2-shifts cannot be a general mechanism that enables rapid isomerization of fluorofullerenes in a broader range of possible cases. This can be illustrated most clearly by a more symmetric process of fluorine atom migration in a $C_{60}F$ radical. It was found, similar to the above case of $C_{60}F_{36}$, that the minimum energy paths for 1,2-shifts of a fluorine atom, as well as for more remote migration thereof, involve complete abstraction of F.

Analogously ruled out were the displacement reactions where an extra fluorine atom attacks a certain site on a carbon cage while another atom undergoes detachment. In general, the activation energy of displacement appears to be rather close to that of migration between the respective sites, not to mention that mere attachment of the said extra fluorine atom would be strongly energetically favorable.

b. Intermolecular Exchange of Fluorine Atoms between Closely Spaced Fullerene Cages. The most probable acts of intermolecular exchange can be divided into three classes depending on the spin multiplicities of the products and reactants. Apparently, the most energy consuming must be hopping of fluorine atom from one stable closed-shell molecule onto another yielding two open-shell doublet species. The inverse process of creation of two singlet molecules from two radicals can be expected to be thermodynamically favorable and hence of much lower activation energy. An intermediate case is represented by exchange of a fluorine atom between a closed-shell molecule and a radical particle.

As an example of formation of two radical species from two stable molecules that may take place during the solid phase fullerene fluorination, we considered an interaction between C_3-$C_{60}F_{36}$ and C_{60} yielding $C_{60}F_{35}$ and $C_{60}F$, where the fluorine atom transferred is the one involved in the above-mentioned isomerization into C_1-$C_{60}F_{36}$. In Figure 3a we show the calculated geometry of the transition state of fluorine atom exchange where the fluorine atom is predictably shifted toward formation of a less stable radical pair. The calculation has yielded a surprisingly low activation energy value of 110 kJ/mol for the direct process and expectably lower 10 kJ/mol for the inverse fluorine transfer. In other words, there occurs an efficient compensation of the energy of a breaking bond by formation of a new one with a neighboring molecule, which decreases the activation barrier almost three times with respect to the typical energy of C_{60}−F homolysis. This immediately points to a possible pathway of solid phase isomerization of fullerene fluorides: (i) transient transfer of a fluorine atom to a neighboring molecule of C_{60} or some lower C_{60} fluoride that has sufficiently large free regions on its carbon cage followed by (ii) rotational reorientation of

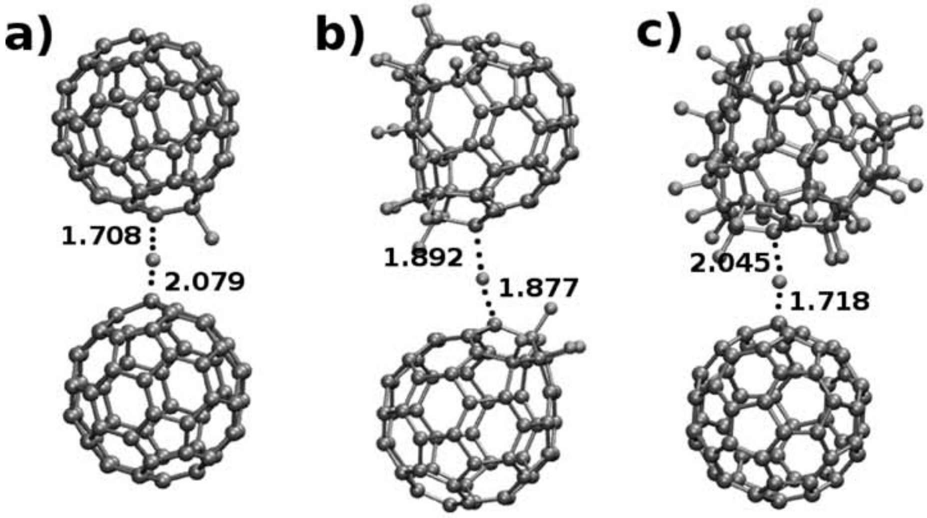

Figure 3. Optimized transition state geometry for fluorine transfer between (a) C_{60} and $C_{60}F_2$, (b) $C_{60}F_6$ and $C_{60}F_{17}$, and (c) C_{60} and $C_{60}F_{36}$.

the two fullerene molecules and, ultimately, (iii) return of the said atom onto a molecule of origin but to a different carbon site.

The observations made for $C_{60}F_{36}$ and C_{60} perfectly reproduce for a simpler pair of $C_{60}F_2$ and C_{60} shown in Figure 3b. The activation energy for both direct and inverse exchange processes is only marginally (within 10 kJ/mol) higher. It has to be noted that the ~100 kJ/mol heat of formation of a pair of closed-shell molecules from a respective pair of radicals provides a quantitative estimate as to what extent attachment of a fluorine atom to a fluorofullerene radical is more favorable than to a stable closed-shell molecule.

Not surprisingly, exchange of a fluorine atom between a closed-shell and a radical fluorofullerene is characterized by even lower activation energy and more symmetric transition states. An example of such fluorine atom hopping between $C_{60}F_6$ and $C_{60}F_{17}$ is shown in Figure 3c. The activation barriers decrease here to 80−85 kJ/mol, suggesting the processes of this kind to be the most probable easy going.

c. Possible Rearrangement Pathways of Fluorinated Fullerenes in Solution. Remarkable electron-withdrawing properties of fluorofullerene molecules point to other conceivable methods of their isomerization such as via interaction with nucleophiles and donor molecules or by fluorine migration in the negatively charged states. Indeed, fluorine abstraction from fluorofullerenes upon double or multiple negative charging, most probably in the form of a fluoride anion, has been observed under the conditions of electrochemical experiments and electrospray mass spectrometry.[12,35,36]

Consideration of singly negatively charged fluorofullerenes reveals certain but insufficient facilitation of fluorine migration compared to neutral molecules. In isolated radical anions like $C_{60}F_{36}^-$, more favorable is abstraction of a fluorine atom rather than that of a fluoride anion since the $C_{60}F_{35}$ radicals were calculated to have a much increased electron affinity of about 4.5 eV. Though the said abstraction of a fluorine atom from $C_{60}F_{36}^-$ is more favorable than from neutral $C_{60}F_{36}$ as it leaves stable closed-shell $C_{60}F_{35}^-$, the respective binding energy still exceeds 250 kJ/mol. Abstraction of F^- may be, of course, favored by solvation effects, but that may require too polar nucleophilic solvents with the potential capability of solvolytic destruction of fluorinated fullerenes, which is known, for example, to be instantly induced by negligible traces of water.[13] In isolated $C_{60}F_{35}^-$-like closed-shell anions themselves, abstraction of a fluorine atom and abstraction of a fluoride anion become comparable in energy but this energy again exceeds 300 kJ/mol.

More interesting and promising are doubly charged systems like $C_{60}F_{36}^{2-}$ or $C_{60}F_{48}^{2-}$ that instantly eliminate F^- upon their second reduction.[12,37] Our gas phase DFT calculations predict such elimination to be ca. 120 kJ/mol endothermic, but, as is suggested by the observations of refs 12 and 37, the strength of solvation effects due to F^- is likely to stabilize the dissociated state even in aprotic organic solvents. In agreement with the said experimental observations, the DFT gas phase value for the barrier of elimination of F^- from $C_{60}F_{36}^{2-}$was found to be only 165 kJ/mol. This value that can be regarded as an estimate from above for the liquid phase conditions is much lower than in singly charged and noncharged systems. Moreover, in the case of fluorofullerene dianions, we ultimately observed a possibility of intermolecular migration of F^- near the carbon cage surface with somewhat lower barriers of 130−140 kJ/mol even when final products are less energetically stable than the initial molecules. Thus, the available experimental and theoretical data give evidence for worthiness of investigation, if not feasibility, of isomerization of fluorofullerenes via (i) electrochemical formation of fluorofullerene dianions and their instant dissociation and (ii) fluoride by fluoride S_N2' substitution in the monoanions thus formed in a manner suggested by Taylor et al.[13]

Following the observations of ref 13, it is also interesting to discuss S_N2' substitution in noncharged systems. The most appealing example in this respect is a two-stage mechanism of eqs 1 and 2 that might explain the above-discussed isomerization of C_1- and C_3-$C_{60}F_{36}$ reported in ref 23.

$$C_1\text{-}C_{60}F_{36} + H_2O \rightarrow C_{60}F_{35}OH + HF \tag{1}$$

$$C_1\text{-}C_{60}F_{35} + HF \leftrightarrow C_3\text{-}C_{60}F_{35} + HF \tag{2}$$

In parts a and b of Figure 4, we show the calculated energy profiles and local stationary and transition state geometries for these two S_N2' reactions. Virtually equal activation energies of 100 kJ/mol evidence that the described reactions can indeed be realized at moderate temperatures. However, because of pronounced thermodynamic favorability of hydrolysis, it seems

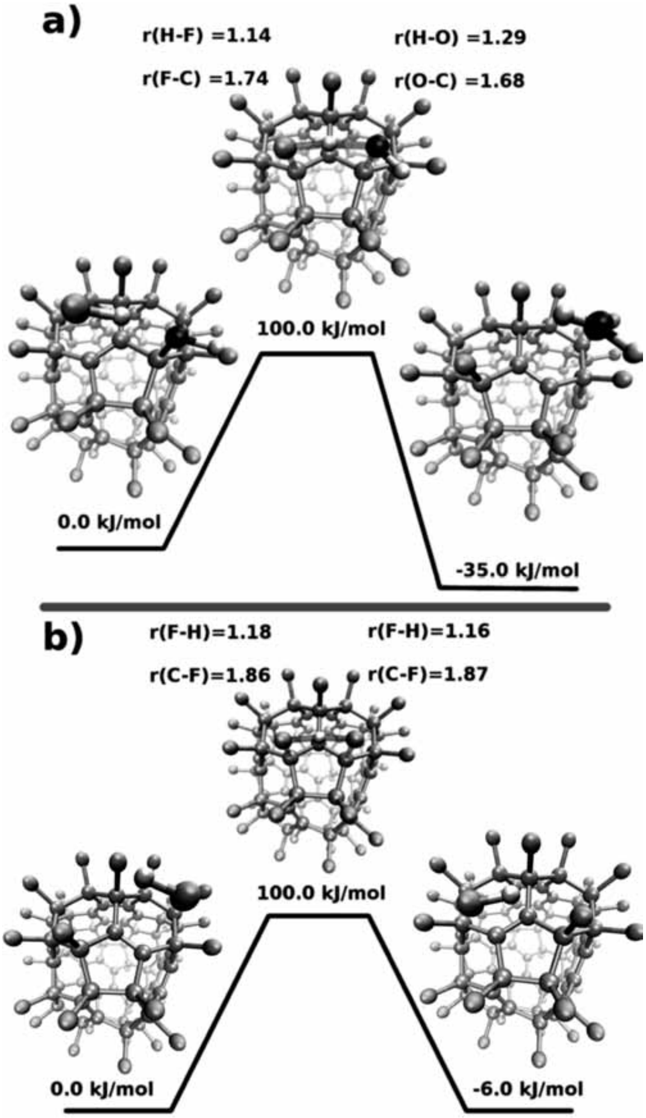

Figure 4. Scheme of two-stage water-assisted $C_{60}F_{36}(C_1)-C_{60}F_{36}(C_3)$ isomerization (see text for details). Geometric parameters (angstrom) are presented for activated complex: (a) $-C_{cage}...F...H...O...C_{cage}-$; (b) $-C_{cage}..\ .F..\ .H..\ .F..\ .C_{cage}-$.

preferable to induce directly the second stage by addition of HF avoiding moisture to a maximum possible extent.

Finally, in view of our experience of electrospray ions generation in ref. 36 and some evidence of their isomerization provided therein, we have considered a fluorine migration pathway involving formation of an ion pair with an organic donor molecule, the fluorine atom being transiently transferred onto the said donor in an exchange for the donated electron. Similarly to the above-discussed case of migration between two fullerene molecules, return of the fluorine atom to a different free site on a fullerene cage would thus effect an act of isomerization as shown by eq. 3 where D denotes a donor molecule.

$$[C_{60}F_{2n}(\text{isomer I})]^{\delta-}\cdot D^{\delta+} \leftrightarrow [C_{60}F_{2n-1}]^{-}\cdot[D-F]^{+} \leftrightarrow [C_{60}F_{2n}(\text{isomer II})]^{\delta-}\cdot D^{\delta+} \quad (3)$$

Again, C_3-$C_{60}F_{36}$ was chosen as a model system, while the donor molecule considered was *N*,*N*,*N′*,*N′*-tetramethyl-1,4-phenylenediamine (TMPD), with an ionization potential of 6.1 eV.[38] In Figure 5 we present the energy profile for fluorine atom transfer onto a donor molecule and the corresponding evolution of the two principal C−F coordinates of this process, as well as transition state geometry. Already in the stationary state of the $C_{60}F_{36}$*TMPD complex, the degree of charge transfer reaches 0.4. In the $C_{60}F_{35}$*TMPD−F state, this value further increases to 0.7, manifesting favorability of stabilization of $C_{60}F_{35}$ in a closed-shell anionic state. The activation barrier for fluorination of TMPD was calculated to be only 100 kJ/mol, i.e., comparable to above-discussed case of fluorine hopping between two fullerene molecules. The inverse process, return of fluorine atom onto $C_{60}F_{35}$, required ca. threefold lower activation energy. Perhaps, in a solution phase one can expect somewhat higher stabilization of the more polar $C_{60}F_{35}$*TMPD−F state and corresponding lowering of the activation barrier in the forward direction. Moreover, the shape of dependence between the $C_{60}F_{35}$...F and TMPD...F distances shown in Figure 5 suggests that the activation energy of fluorine atom transfer could be decreased even further if not for the obvious steric effects that prevent the two molecules from approaching each other more closely.

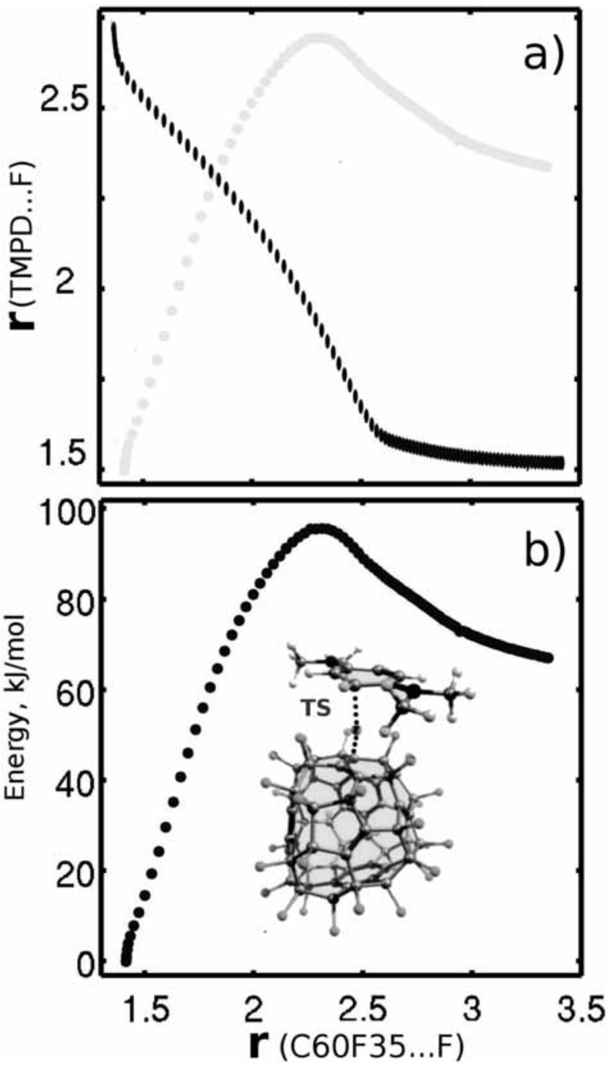

Figure 5. Evolution of principal C...F distances (a) and energy profile (b) for fluorine atom transfer between $C_{60}F_{36}$ and TMPD.

To demonstrate that it is the charge transfer that plays the key role in the process in question, we replaced TMPD with ortho-dichlorobenzene (DCB), a common solvent for fullerene derivatives with no donor properties and hence quite negligible

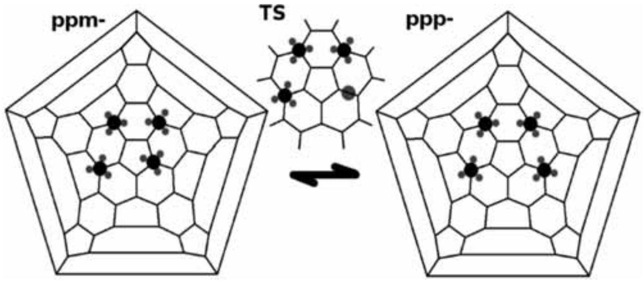

Figure 6. Schlegel diagram representation of the ppm−ppp transformation of $C_{60}(CF_3)$. TS denotes transition state.

degree of charge transfer in the $C_{60}F_{36}$*DCB state. Not surprisingly, the activation energy for formation of $C_{60}F_{35}$*DCB−F via fluorine transfer increased twice to ca. 200 kJ/mol despite more pronounced observable charge transfer of 0.4 in this final state.

Unfortunately, synthetic practicability of donor-induced rearrangements may be compromised by various side processes of which the most obvious is further defluorination of a fluorofullerene. As an example, one can consider transformation of the $C_{60}F_{35}$*TMPD−F complex into $C_{60}F_{34}$*fluoro-TMPD + HF where fluoro-TMPD stands for a TMPD molecule that is singly fluoro-substituted at the benzene ring. Defluorination of the original $C_{60}F_{36}$*TMPD into $C_{60}F_{34}$*fluoro-TMPD + HF appears to be slightly thermodynamically favorable by 22 kJ/mol, which result is in agreement with our mass spectrometric observations of partial loss of fluorine in fluorofullerene−TMPD solutions.[33] Nevertheless, interactions of fluororfullerenes with donors may be regarded as a potential new direction in their chemistry where, for example, the resulting anions may serve as long-living intermediates.

2. Trifluoromethylated Fullerenes.

a. Intramolecular Shifts of CF_3 Groups. In trifluoromethylated derivatives of C_{60}, analogously to fluorofullerenes, only 1,2-shifts of CF_3 groups were found to have pathways more energetically favorable than almost complete bond dissociation followed by reattachment to a desired new site. Whereas the activation barriers for the said detachment−reattachment mechanism are roughly equal to bond dissociation energy exceeding in most cases 200 kJ/mol, 1,2-shifts of CF_3 groups may be characterized by surprisingly low activation barriers when the respective isomers exhibit dramatic difference in stability, even lower than in the above-discussed case of fluorofullerenes. Very illustrative is transition of the para−para−meta (ppm) isomer of $C_{60}(CF_3)_4$ into a para−para−para (ppp) one shown in Figure 6. The ppm structure is 184 kJ/mol less stable than the ppp one, and this remarkable asymmetry makes the CF_3 migration barrier toward the ppp structure as low as 40 kJ/mol. Thus, similar to fullerene fluorides, intramolecular CF_3 shifts in trifluoromethylated fullerenes provide a mechanism to destroy too energetically unfavorable structures, which results in narrower relative energy distributions of the products. However, those 1,2-shifts that couple isomers of comparable energy are, again, too strongly hindered. This can be demonstrated by a symmetric case of migration of a CF_3 group in $C_{60}CF_3$ between the adjacent sites. The activation energy of ca. 210 kJ/mol roughly equals the energy of CF_3 abstraction.

b. Intermolecular Exchange of CF_3 Groups. Remarkably low activation barriers for intermolecular migration of fluorine atoms between fluorofullerenes motivated us to consider similar processes for trifluoromethylated derivatives of C_{60}. However, the results obtained for this latter case appeared to be strikingly different. The reasons for that can be easily seen from transition state geometry for CF_3 group exchange between para-$C_{60}(CF_3)_2$ and C_{60} presented in Figure 7. The CF_3 group must undergo inversion to be able to form a new bond with the target fullerene cage. As a result, in its transition configuration the CF_3 group is planar like in its free state, and both cleaving and newly forming bonds are virtually nonexistent. Thus, such intermolecular processes are effectively equivalent to sequential detachment and reattachment and have, as such, no advantage over intramolecular CF_3 migration. This is clearly illustrated by the activation energy values for the system shown in Figure 7: even in the thermodynamically favorable direction, that is, formation of para-$C_{60}(CF_3)_2$ and C_{60} from two $C_{60}CF_3$ radicals, the activation barrier was calculated to be 210 kJ/mol, while in the other direction it is an additional 100 kJ/mol higher. Hence intra- and intermolecular transformation of stable trifluoromethylated derivatives of C_{60} are likely to be of comparable rate, both being much slower than isomerization of fullerene fluorides via intermolecular mechanisms, which is clearly reflected by extensive isomerism of the synthetically available $C_{60}(CF_3)_n$ (as well as $C_{70}(CF_3)_n$) compounds.

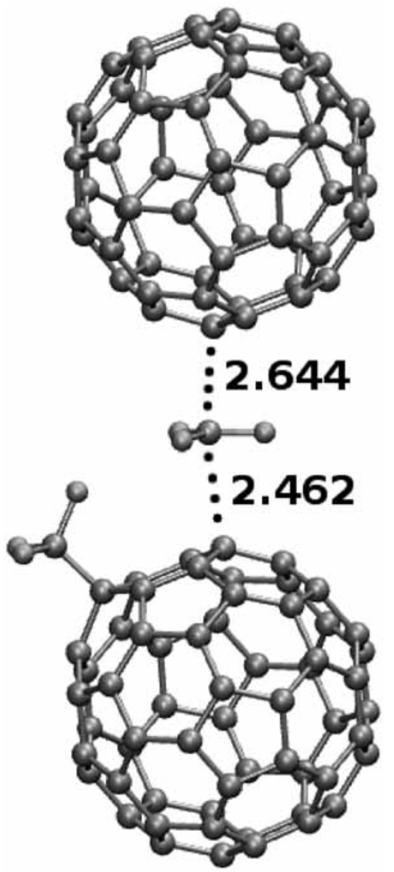

Figure 7. Optimized transition state geometry for CF_3 group hopping between $C_{60}(CF_3)_2$ and C_{60}.

Conclusion

Fluorine and CF_3 addends in functionalized fullerenes demonstrate very different behavior with regard to isomerization of addition motifs. While a fluorine atom can relatively easily relink to a neighboring fullerene molecule, CF_3 groups first have to undergo appropriate inversion so that the dissociation energy of a cleaving bond cannot be instantly compensated by any exothermic effect. As a result, fluorofullerenes are known to selectively form a very narrow range of isomers believed to be equilibrated thermodynamically, while in trifluororomethylated fullerenes any relatively stable structure becomes almost a "dead end", which isomerizes, at best, much more slowly, and, in addition, concurrently with thermal decomposition.

It likely that the observations presented relate to a broader range of fullerene derivatives than described here. In particular, there must be much similarity between CF_3 groups and other alkyl or fluoroalkyl addends, while the behavior of fluorinated fullerenes can be shared, under appropriate conditions, by fullerene hydrides and chlorides. However, highly electron-withdrawing fluorofullerenes have a completely unique capability of forming reactive doubly charged states and interacting with nucleophiles and donors more easily than any other class of fullerene derivatives. One can expect these yet poorly explored reactions to find their place in the synthetic practice of fullerene chemistry.

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