Journal of Fluorine Chemistry 143 (2012) 103–108

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Solution-phase perfluoroalkylation of C_{60} leads to efficient and selective synthesis of bis-perfluoroalkylated fullerenes

Igor V. Kuvychko, Steven H. Strauss, Olga V. Boltalina *

Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA

A R T I C L E I N F O

Article history:
Received 2 February 2012
Received in revised form 20 April 2012
Accepted 26 April 2012
Available online 4 May 2012

Dedicated to David O'Hagan on the occasion of his receiving ACS Award for Creative Work in Fluorine Chemistry.

Keywords:
Fullerene
C_{60}
Perfluoroalkylation
R_FI
Perfluoroalkyl radicals

A B S T R A C T

A solution-phase perfluoroalkylation of C_{60} with a series of R_FI reagents was studied. The effects of molar ratio of the reagents, reaction time, and presence of copper metal promoter on fullerene conversion and product composition were evaluated. Ten aliphatic and aromatic R_FI reagents were investigated (CF_3I, C_2F_5I, n-C_3F_7I, i-C_3F_7I, n-C_4F_9I, $(CF_3)(C_2F_5)CFI$, n-$C_8F_{17}I$, $C_6F_5CF_2I$, C_6F_5I, and 1,3-$(CF_3)_2C_6F_3I$) and eight of them (except for C_6F_5I and 1,3-$(CF_3)_2C_6F_3I$) were found to add the respective R_F groups to C_{60} in solution. Efficient and selective synthesis of $C_{60}(R_F)_2$ derivatives was developed.

Published by Elsevier B.V.

1. Introduction

The chemistry of perfluoroalkylfullerenes (PFAFs) has been rapidly evolving in recent years. Many isomerically pure derivatives of C_{60} [1–5], C_{70} [6–9], hollow higher fullerenes [10–13], and endometallofullerenes [14–16] have been synthesized, isolated, and studied by various techniques. Perfluoroalkylfullerenes were shown to be attractive electron acceptors due to their high thermal and chemical stability, reversible electrochemical behavior in solution, and a broad range of their first reduction potentials [1,8,17]. It was also shown that PFAFs can be further derivatized chemically to form donor–acceptor diads and potentially other complex molecular systems [18,19]. The vast majority of PFAF syntheses described in the literature relied on heterogeneous high-temperature reactions between fullerenes and $R_F^{\bullet}$ precursors (e.g., R_FI or $AgOOCCF_3$, see Refs. above). Such conditions typically favor the formation of PFAFs with a large number of R_F substituents, with simple bis-derivatives fullerene$(R_F)_2$ either absent from crude reaction mixtures or present in trace amounts [4,5,20,21]. Only 1,7-$C_{60}(CF_3)_2$ [20,22], 1,7-$C_{60}(C_2F_5)_2$ [23], and 1,7-$C_{60}(i$-$C_3F_7)_2$ [24] have been isolated and characterized using high-temperature heterogeneous synthetic methods. It is notable that previous studies of C_{60} halogenation demonstrated that selective synthesis of simple bis-derivatives $C_{60}Hal_2$ (Hal = F, Cl, and Br; iodofullerenes have not been reported) is difficult to achieve while many multi-substituted $C_{60}Hal_n$ have been prepared (e.g., $C_{60}F_{18}$, $C_{60}F_{36}$, $C_{60}F_{48}$, $C_{60}Cl_6$, $C_{60}Cl_{24}$, and $C_{60}Br_{24}$). For example, single isomers of $C_{60}F_2$ [25] and $C_{60}Cl_2$ [26] were only prepared as minor products; $C_{60}Br_2$ has never been observed experimentally.

Recently we reported a fundamental study of substituent effects in a series of 1,7-$C_{60}(R_F)_2$ compounds with R_F = CF_3, C_2F_5, n-C_3F_7, i-C_3F_7, n-C_4F_9, s-C_4F_9 (secondary-$CF(CF_3)(C_2F_5)$), and n-C_8F_{17} using cyclic voltammetry, low-temperature anion photoelectron spectroscopy, and DFT calculations [23]. The similarity of the first reduction potentials of these compounds, their largely intact π-systems, and differences in their physical properties (e.g., different solubility [23] and crystal packing [23,24,27]) makes them an intriguing series of compounds that may be used to study the effects of morphology of the active polymer-fullerene blend layers on the function of microelectronic devices such as solar cells. Except for 1,7-$C_{60}(R_F)_2$ compounds with R_F = CF_3 and C_2F_5, all other 1,7-$C_{60}(R_F)_2$ compounds in that study were prepared using a solution-phase perfluoroalkylation technique [23]. In this paper we report the development and optimization of this synthetic method.

---

* Corresponding author.
E-mail addresses: kuvychko@lamar.colostate.edu (I.V. Kuvychko), steven.strauss@colostate.edu (S.H. Strauss), olga.boltalina@colostate.edu, ovbolt@lamar.colostate.edu (O.V. Boltalina).

0022-1139/$ – see front matter. Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.jfluchem.2012.04.014

Krusic et al. were the first to explore a solution-phase fullerene perfluoroalkylation in 1991 [28]. They observed the formation of $C_{60}(CF_3)^\bullet$ radical by ESR spectroscopy in a reaction of C_{60} with $(CF_3CO_2)_2$ under UV irradiation in Freon-113 [28]. In 1993 Fagan et al. described fullerene perfluoroalkylation with several R_F radical sources (CF_3I, C_2F_5I, n-C_3F_7I, n-$C_6F_{13}I$, $(CF_3CO_2)_2$, $(C_2F_5CO_2)_2$, and (n-$C_3F_7CO_2)_2$) in various solvents (1,2,4-trichlorobenzene, benzene, hexafluorobenzene, *tert*-butylbenzene, and chlorobenzene) at elevated temperatures or under UV irradiation [29]. Complex mixtures of $C_{60,70}(R_F)_nH_m$ products with n up to 16 and m up to 30 have been prepared but no single isomers were isolated [29]. Several papers described ESR studies of various $C_{60}(R_F)^\bullet$ and $C_{70}(R_F)^\bullet$ species formed in solutions of aromatic and aliphatic solvents (benzene, toluene, *tert*-butylbenzene, and methylcyclohexane) from corresponding bare-cage fullerenes and various R_F radical precursors (R_FI, R_FBr, and $(R_FCO_2)_2$) at elevated temperatures or under UV irradiation [30–33]. In 1993 Yoshida et al. reported that a reaction of C_{60} with $(R_FCO_2)_2$ ($R_F = CF_3$ and n-C_3F_7) in deoxygenated chlorobenzene solution at 40 °C resulted in formation of 1,7-$C_{60}R_F(OH)$ alcohol and 1,9-$C_{60}O_2CR_F(OH)$ "orthoester" ($CR_F(OH)$ moiety connected to C_{60} via two oxygen atoms forming a 1,3-dioxolane cycle) [34]. Interestingly, in 1994 the same group reported a reduction of $(C_{60}R_F)_2$ dimer by Bu_3SnH to form $C_{60}R_FH$ [35]; they claimed that the dimer was prepared and reported in their 1993 paper using the solution-phase reaction of C_{60} with $[R_FCO_2]_2$ (the dimer formation or isolation was not mentioned in that paper) [34]. In 1999 Yoshida and co-workers reported an optimized procedure for $(C_{60}R_F)_2$ synthesis based on a reaction of C_{60} with R_FI ($R_F = n$-C_3F_7, n-C_4F_9, n-C_6F_{13}) in 1,2-dichlorobenzene (ODCB) solution in the presence of hexabutylditin or hexamethylditin under irradiation with metal-halide lamp [36]. A solution-phase synthesis of a mixture of perfluorohexylated species with an average composition $C_{60}(C_6F_{13})_{\sim 5}$ in a reaction of C_{60} with n-$C_6F_{13}I$ in 1,2,4-trichlorobenzene at 200 °C was reported in 1999, but the elemental analysis was the only characterization method used in that study [37].

In this work we studied the solution-phase perfluoroalkylation of C_{60} in detail using HPLC analysis and mass spectrometry with the aim of selective and efficient preparation of $C_{60}(R_F)_2$ derivatives and other PFAFs. Multiple small-scale experiments were carried out in order to ascertain the effects of the molar ratio of the reagents, reaction time, and copper metal promoter on the product composition and C_{60} conversion.

2. Materials and methods

2.1. Solvents and reagents

The solvents toluene (Fisher Scientific; HPLC grade), n-heptane (Fisher Scientific; HPLC grade), acetonitrile (Fisher Scientific; HPLC grade), dimethyl sulfoxide (Fisher Scientific; ACS grade), 1,2-dichlorobenzene (ODCB; Acros Organics; ACS grade), chloroform-*d* (99.8% D, Cambridge Isotope Laboratories, Inc.) were used as received. The compounds C_{60} (99.9%, Term-USA), R_FI ($R_F = CF_3$, C_2F_5, n-C_3F_7, i-C_3F_7, n-C_4F_9, s-C_4F_9, n-C_8F_{17}, $CF_2C_6F_5$, C_6F_5, 3,5-$(CF_3)_2C_6F_3$) (SynQuest Labs), and copper powder (Fisher Scientific; 325 mesh; electrolytic grade) were used as received.

2.2. Instruments

HPLC analysis and separation was accomplished using Shimadzu HPLC instrumentation (CBM-20A control module, SPD-20A UV-detector set to 300 nm detection, LC-6AD pump, manual injector valve) equipped with a 10-mm I.D. × 250 mm semipreparative Cosmosil Buckyprep column (Nacalai Tesque, Inc.) Atmospheric-pressure chemical ionization (APCI) mass spectra were recorded using Agilent Technologies Model 6210 TOF spectrometer with APCI source. The carrier solvent was acetonitrile with 1% toluene; PFAF samples were injected as toluene solutions. Fluorine-19 NMR spectra were recorded on Varian 400 MR spectrometer at 376 MHz frequency ($CDCl_3$ solvent was used).

2.3. Perfluoroalkylation experiments

Aliquots of 500 μL of a stock solution of C_{60} in ODCB (13.8 mM) were transferred into a Pyrex glass ampoule (O.D. = 8.0 mm; I.D. = 5.0 mm; L = 140 mm; V = 2.7 mL) containing ca. 500 mg of copper powder. An R_FI reagent was then added via a gas-tight syringe (for small excesses of 6 equiv. a diluted stock solution of i-C_3F_7I in ODCB was used), and the solution was diluted to 1.0 mL with pure ODCB (in several experiments 250 μL of DMSO were also added prior to the ODCB dilution). The gaseous reagents CF_3I (b.p. = −21.85 °C [38]) and C_2F_5I (b.p. = 12.5 °C, vendor data) were measured volumetrically and transferred on a vacuum line equipped with a calibrated volume and an electronic manometer (MKS Instruments Baratron vacuum gauge, 0–1.3 bar). In these two cases the 500 μL stock solution of C_{60} was diluted to 1.0 mL volume with ODCB prior to the addition of CF_3I and C_2F_5I. In all cases the ampoules were degassed three times using a freeze-pump–thaw technique, frozen in liquid nitrogen, and flame-sealed under vacuum. The ampoules were heated at 180 °C in a tube furnace, then cooled down, frozen in liquid nitrogen, and opened. The crude reaction mixtures were evaporated under vacuum to dryness (reaction mixtures containing DMSO were washed with water three times prior to drying). The dry residues were dissolved in 10.0 mL of toluene, filtered, and analyzed using HPLC (100 μL sample injections) and APCI mass spectrometry.

3. Results

The effects of the reaction time and the molar ratio of the reagents on C_{60} conversion and product distribution were studied using reactions between C_{60} and i-C_3F_7I. The reaction conditions were kept the same except for varying amounts of i-C_3F_7I (6, 18, 54, and 162 equiv.) and reaction time (1 and 3 days). In all cases reactions were carried out in degassed 1,2-dichlorobenzene (ODCB) solution at 180 °C in sealed glass ampoules of the same volume (2.7 mL). A large excess of copper metal powder (500 mg; 7.9 mmol) was added to each of the reaction mixtures prior to degassing and heating. In all solution-phase experiments described in this work the total volume of the reaction mixture was 1.0 mL and the initial concentration of C_{60} was 6.9 mM. The crude reaction mixtures were filtered, evaporated to dryness, and dissolved in 10.0 mL of toluene. These solutions were analyzed by HPLC using pure toluene as the primary eluent and the HPLC traces were stacked for direct comparison, see Fig. 1 (injection volume was 100 μL; retention time $t_R(C_{60})$ = 8.7 min; t_R(1,7-$C_{60}(i$-$C_3F_7)_2$) = 5.7 min [23]). Pure toluene was not effective for the analysis of $C_{60}(i$-$C_3F_7)_{n>4}$ products due to their short retention times; for such mixtures pure heptane was used instead to provide adequate peak separation (see inserts in Fig. 1). The crude products were also analyzed by negative-ion APCI mass spectrometry which showed distributions of peaks corresponding to the $C_{60}(C_3F_7)_n^-$ anions with n = 1–8. The numbers shown to the immediate right of the HPLC traces in Fig. 1 represent the distributions of the $C_{60}(C_3F_7)_n^-$ peaks observed in the NI-APCI mass spectra of the corresponding products (the large-font numbers represent the most intense peaks in the spectra). It is notable that no evidence of the formation of dimeric species $(C_{60}R_F)_2$ were observed throughout our study (neither by mass spectrometry nor by HPLC analysis) [34–36].

The effect of the copper metal was studied in a separate experiment. A sample of C_{60} was allowed to react with 162 equiv.

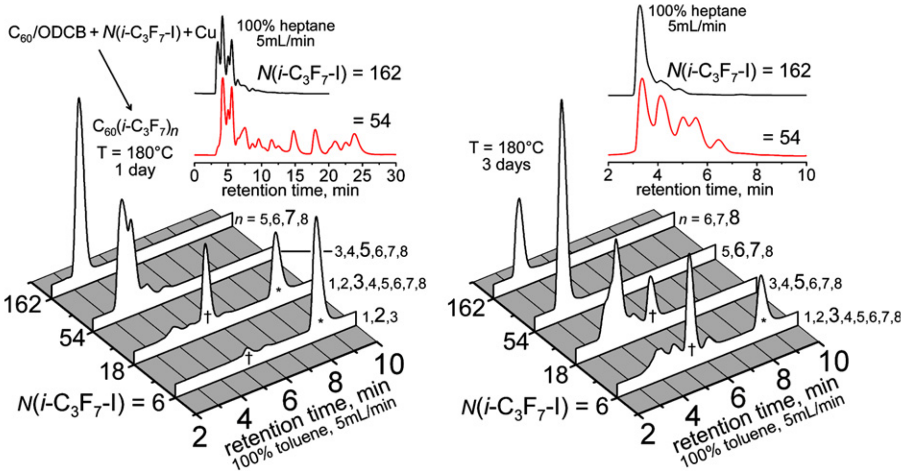


Fig. 1. The HPLC analysis of several C_{60} + $N(i\text{-}C_3F_7I)$ reactions carried out in ODCB solution in the presence of copper powder at 180 °C. The peaks at t_R = 5.7 min marked with daggers corresponds to 1,7-$C_{60}(i\text{-}C_3F_7)_2$; the peaks at t_R = 8.7 min marked with stars correspond to unreacted C_{60}. The numbers on the right-hand side of the HPLC traces show the distribution of $C_{60}(C_3F_7)_n^-$ anions observed in the NI-APCI MS analysis of the corresponding samples (the numbers given with a large font correspond to the most intense ion in the spectra). The inserts show the HPLC traces of four samples acquired using 100% heptane eluent.

of i-C_3F_7I in ODCB solution at 180 °C for 3 days *without* any copper present. Upon the workup the reaction mixture was found to contain a significant amount of iodine (no iodine was observed in any of the reactions carried out in the presence of copper). The product was analyzed by HPLC and NI-APCI mass spectrometry; the composition of the PFAF products formed in a three-day reaction between C_{60} and 162 equiv. of i-C_3F_7I without copper is similar to the products formed in one-day reaction of C_{60} and 54 equiv. of i-C_3F_7I with copper (see Figs. 1 and 2).

Several reactions between C_{60} and 54 and 18 equiv. of CF_3I and 18 equiv. of i-C_3F_7I were also carried in 25/75 (v/v) DMSO/ODCB mixture at 180 °C, both with and without copper metal. The crude reaction mixtures were washed with water several times to remove DMSO; then they were treated analogously to the crude products prepared in pure ODCB. The resulting products quickly decomposed upon their exposure to air (the freshly filtered solutions quickly changed color and became murky with white insoluble precipitates) which made them impossible to analyze using conventional HPLC or mass spectrometry.

The reactivity of different R_FI reagents (R_F = CF_3, C_2F_5, n-C_3F_7, i-C_3F_7, n-C_4F_9, s-C_4F_9, n-C_8F_{17}, $CF_2C_6F_5$, C_6F_5, and 3,5-$(CF_3)_2C_6F_3$) toward C_{60} in ODCB solution was also studied; 18 equiv. of the R_FI reagents were used in all cases and the reaction time was one day.

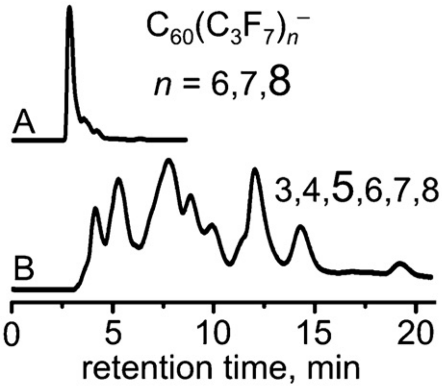


Fig. 2. HPLC and NI-APCI mass spectrometry analysis of the products of the reaction of C_{60} with 162 equiv. of i-C_3F_7I reagent in ODCB solution at 180 °C for three days with copper metal powder (A) and without copper metal powder (B). The n values represent the distributions of $C_{60}(C_3F_7)_n^-$ species observed in the NI-APCI mass spectra.

The resulting reaction mixtures were studied by HPLC using pure toluene as the eluent, see Fig. 3 (50/50 (v/v) toluene/heptane mixture was also used for the perfluorobenzylated products, see the insert in Fig. 3). The aliphatic R_FIs and perfluorobenzyl iodide yielded the corresponding $C_{60}(R_F)_n$ products (this was confirmed by NI-APCI mass spectrometry, figures not shown). No reaction was observed for the aromatic R_FI reagents C_6F_5I and 3,5-$(CF_3)_2C_6F_3I$.

It is notable that most of the C_{60} reagent precipitated out of the hot ODCB after several hours of heating when CF_3I, 3,5-$(CF_3)_2C_6F_3I$, or C_6F_5I were used. In these cases the hot ODCB solutions changed from a deep magenta to a pale-pink color and black precipitates were formed. After cooling the black precipitates were redissolved forming the deep magenta-colored solutions typical of C_{60} (the HPLC analysis also confirmed that the C_{60} reagent was unchanged, see Fig. 3). These observed precipitations are consistent with the experimentally studied anomalous temperature dependence of C_{60} solubility in organic solvents including ODCB [39,40].

Finally, we performed several experiments with ca. 0.027 bar of gaseous C_2F_5I, n-C_3F_7I, and i-C_3F_7I and C_{60} in a GTGS reactor [22]. The reaction between C_2F_5I and C_{60} without copper metal at ca. 480 °C was largely unsuccessful due to a very low C_{60} conversion (less than 5%) [23]. In order to improve the conversion of C_{60} we performed an experiment with the use of Cu powder as a promoter but it led to a high abundance of $C_{60}(C_2F_5)_n$ products with $n > 2$ ($P(C_2F_5I)$ = 0.021–0.016 bar; T = 430 °C; the yield of 1,7-$C_{60}(C_2F_5)_2$ was ca. 1–2 mol%; see Supporting Information of Ref. [23]). Attempts to use a GTGS reactor to carry out reactions with n-C_3F_7I and i-C_3F_7I did not yield any PFAF products, and all starting C_{60} was recovered unchanged both with and without copper metal powder; a range of the reaction temperatures up to 500 °C was explored.

4. Discussion

Reactions involving perfluoroalkyl radicals are commonly used for a preparation of a variety of organofluorine compounds [41]. Substitution of aromatic hydrogen atoms by $R_F^\bullet$ radicals has been used to prepare aromatic compounds bearing various R_F groups [42–46] (see also [47,48] for similar catalytic processes); addition of $R_F^\bullet$ radicals to alkenes has also been well-studied [49,50]. Thermolysis of R_FI or $(R_FCO_2)_2$ precursors has been commonly used to generate $R_F^\bullet$ radicals (see for example [42,43,46]). The other common method of $R_F^\bullet$ generation relies on a rapid reaction of R_FI

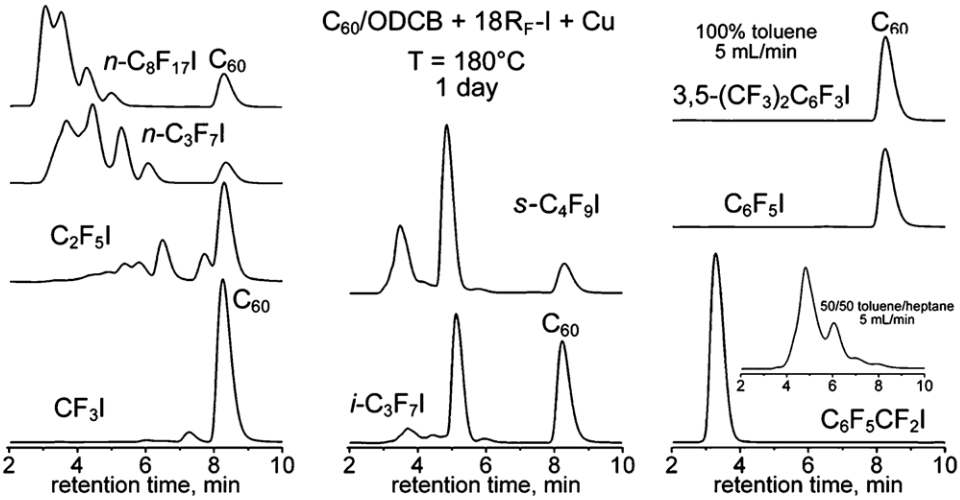


Fig. 3. HPLC analysis of the products of C_{60} reactions with 18 equiv. of various R_FI reagents. Reactions were carried out in ODCB solution in the presence of copper powder at 180 °C for one day.

with $CH_3^\bullet$ or $C_6H_5^\bullet$ radicals formed in situ (in the reaction of acetone with hydrogen peroxide [44] or by photolysis of $(PhCO_2)_2$ [45,51], correspondingly).

The original work by Fagan et al. [29] was the first to employ the addition of perfluoroalkyl radicals to fullerenes leading to a successful synthesis of mixtures of various PFAFs. In that work, $R_F^\bullet$ radicals were formed in situ by thermolysis or UV irradiation of solutions of R_FI or $(R_FCO_2)_2$ radical precursors; $R_F^\bullet$ then reacted with C_{60} (or C_{70}) which acted as a radical trap [29,37]. The formation of radical intermediates $C_{60}(R_F)^\bullet$ was confirmed by ESR spectroscopy [29–33]. Large excess of $R_F^\bullet$ radical precursors were used, resulting in mixtures of highly perfluoroalkylated fullerenes. It is notable that the use of C_6H_6 reaction medium resulted in the formation of some hydrogenated PFAFs [29]. This process was eliminated by the use of fluorinated solvents such as C_6F_6 or Freon-113 [29], but these reactions must have been heterogeneous since fullerenes are practically insoluble in fluorinated solvents [52].

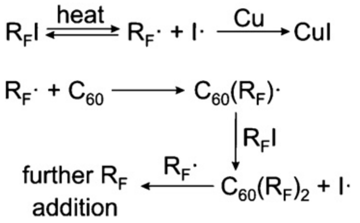
In this study, thermolysis of R_FI reagents was chosen for the generation of $R_F^\bullet$ radicals in order to avoid possible side-reactions of radicals other than $R_F^\bullet$ with C_{60} (e.g., $CH_3^\bullet$ or $C_6H_5^\bullet$ radicals [44,45,51]). Note that $C_{60}I_n$ compounds with covalent C_{60}–I bonds have not been reported; this is believed to be due to the low energy of C_{60}–I bonds [53]. In this work we have not observed any evidence for the formation of persistent $C_{60}(R_F)_nI_m$ species.

The reaction medium was chosen to be 1,2-dichlorobenzene (ODCB) due to several factors. First, C_{60} and other fullerenes and fullerene derivatives are known to be very soluble in ODCB [52] (anomalous temperature dependence of fullerene solubility notwithstanding [39,40]). Second, ODCB has a high boiling point (180 °C) and a relatively low vapor pressure which eliminates the need for high-pressure reactors. Third, it is rather inert toward radical reactions; we have not observed appreciable amounts of fullerene products with substituents other than R_Fs (e.g., hydrogen atoms [29] or aryl groups) or products resulting from a perfluoroalkylation of ODCB. The higher-boiling 1,2,4-trichlorobenzene was also considered, but it is harder to remove under vacuum which complicates workup of the crude products.

Copper metal powder was used to promote the decomposition of R_FI reagents and accelerate fullerene perfluoroalkylation in solution. It was found that C_{60} perfluoroalkylation also takes place without copper metal but the reaction rate was several times slower. Copper metal serves as an iodine scavenger [22], thereby shifting the equilibrium of R_FI dissociation toward the formation of the R_F radicals, see Scheme 1. Even with copper metal present, the decomposition of the R_FI reagents at 180 °C is relatively slow, which necessitated the use of high stoichiometric ratios of the reagents ($n(R_FI)/n(C_{60})$) up to 162 equiv. for some reactions with i-C_3F_7I). It is likely that other metals like Ag and Tl can also be used as iodine scavengers. We have not tested these metals in this work due to their higher price and high toxicity.

It is notable that high-boiling polar solvents like DMSO, DMF, pyridine, and HMPA have been used extensively for solution-phase coupling reactions between aliphatic and aromatic halogenated substrates and R_FI reagents in the presence of copper metal. In such reactions a halogen atom (typically iodine or bromine) is substituted by an R_F group [54–56]. These reactions are likely to involve the initial formation of perfluoroorganocopper intermediates [R_FCu] (formation of such intermediates was shown in several cases, see Refs. above). The use of polar solvents (donor number > 19) is believed to be necessary to minimize the unwanted formation of R_F radicals which decreases the selectivity and yield of the coupling reactions [55]. Fullerenes are practically insoluble in polar solvents [52], so we used 25/75 (v/v) mixture of DMSO and ODCB to carry out fullerene perfluoroalkylation. Air-sensitive products of unknown compositions were formed, therefore this direction was not pursued further. The fact that C_{60} perfluoroalkylation by R_FI in hot ODCB occurs even without any copper metal present (albeit at a slower rate, see above) suggests that the formation of organocuprate reagents is probably not involved in this reaction which is likely to be a simple radical addition.

The solution-phase reaction of i-C_3F_7I with C_{60} in ODCB in the presence of copper showed that molar ratios of these reagents and reaction time have a strong effect on the composition of products, see Fig. 1. A low excess of i-C_3F_7I (6 equiv.) led to a very low C_{60}



Scheme 1. Fullerene perfluoroalkylation in solution (possible chain termination processes and are not shown).

conversion after a one-day reaction. Most of the starting C_{60} was left unchanged but the HPLC analysis and the NI-APCI mass spectrometry showed that a small amount of 1,7-$C_{60}(i\text{-}C_3F_7)_2$ was formed (the single isomer of this compound was isolated earlier from the products of heterogeneous C_{60} perfluoroalkylation, see Ref. [23]). A longer reaction time (three days) led to a better C_{60} conversion and a relatively selective formation of 1,7-$C_{60}(i\text{-}C_3F_7)_2$ with a ca. 25% yield (based on the HPLC analysis). The reaction with 18 equiv. of $i\text{-}C_3F_7I$ over a period of one day led to a lower conversion of C_{60} and a selective formation of 1,7-$C_{60}(i\text{-}C_3F_7)_2$ with a ca. 40% yield. The HPLC analysis and the mass spectrometry also showed that only small amounts of $C_{60}(i\text{-}C_3F_7)_{4,6}$ compounds were formed (highly substituted $C_{60}(R_F)_n$ compounds typically have shorter retention times [21,22]). Higher molar ratios of $i\text{-}C_3F_7I$ to C_{60} and longer reaction time resulted in formation of more highly substituted products. A high excess of $i\text{-}C_3F_7I$ (162 equiv.) used in a three-day reaction, resulted in the formation of a major $C_{60}(i\text{-}C_3F_7)_8$ product as shown by the mass spectrometry. Fluorine-19 NMR spectroscopy of this product suggested it to be a mixture of isomers (figure not shown). This shows that the maximum number of $i\text{-}C_3F_7$ groups that can be added to C_{60} under these conditions is limited to eight ($Max(i\text{-}C_3F_7/C_{60}) = 8$). This lies in agreement with the results of high-temperature heterogeneous reactions between C_{60} and high-pressure gaseous $i\text{-}C_3F_7I$ that also did not produce any products with more than eight $i\text{-}C_3F_7$ substituents (but multiple isomers of $C_{60}(i\text{-}C_3F_7)_{4,6,8}$ were isolated and characterized) [24]. The maximum number of R_F additions to the C_{60} cage depends on the steric demand of the R_F groups. For the smallest R_F group, CF_3, $C_{60}(CF_3)_{22}$ species have been observed experimentally ($Max(CF_3/C_{60}) = 22$) [57]. As the size of the R_F substituents increases, the highest experimentally observed degree of C_{60} perfluoroalkylation decreases ($Max(C_2F_5/C_{60}) = 16$; $Max(n\text{-}C_3F_7/C_{60}) = 12$; see also Ref. [21] for other experimental $Max(R_F/C_{60})$ values).

Reaction conditions that led to a low conversion of C_{60} produced 1,7-$C_{60}(i\text{-}C_3F_7)_2$ with a high degree of selectivity, see Fig. 1. In our experiments it corresponded to 6 and 18 equiv. of $i\text{-}C_3F_7I$ (the high excess implies that not all of this reagent is used up productively during the reaction). The mass spectrometry analysis of the corresponding products showed a wide range of $C_{60}(i\text{-}C_3F_7)_n$ with up to eight substituents were formed. It is notable that no R_F fragmentation was observed in any of the solution-phase reactions described in this work; such fragmentation was observed above 300 °C when longer-chain R_FI reagents were used for heterogeneous perfluoroalkylation of fullerenes [21].

Based on this work we developed several efficient solution-phase syntheses of new 1,7-$C_{60}(R_F)_2$ compounds with $R_F = n\text{-}C_3F_7$, $i\text{-}C_3F_7$, $n\text{-}C_4F_7$, $s\text{-}C_4F_7$, and $n\text{-}C_8F_{17}$ which are described in a separate paper [23]. After some optimization of the reaction conditions and HPLC-based separation procedures these compounds were prepared with 10–20 mol% yields, see Ref. [23] for synthetic details and analytical data of the isolated compounds. Higher yields may be achievable; e.g., ca. 40% yield (based on the HPLC trace integration) was achieved in a small-scale synthesis of 1,7-$C_{60}(i\text{-}C_3F_7)_2$, see Fig. 1 ($N(i\text{-}C_3F_7I) = 18$; reaction time = 1 day). In the corresponding large-scale experiments the yields varied between 10 and 20% depending on small variations of the heating regime and other reaction parameters such as reactor size and geometry [23]; the yields and conversion were kept intentionally low to suppress the formation of $C_{60}(R_F)_{n>2}$ which, unlike unreacted C_{60}, cannot be recycled.

5. Conclusions

The results presented in this work indicate that homogeneous perfluoroalkylation of C_{60} is currently the most efficient method for preparation of bis-$C_{60}(R_F)_2$ derivatives with a variety of different R_F groups. Currently it is the only method of synthesis for 1,7-$C_{60}(R_F)_2$ with $R_F = n\text{-}C_3F_7$, $n\text{-}C_4F_9$, $s\text{-}C_4F_9$, and $n\text{-}C_8F_{17}$. Lower reaction temperatures used for solution-phase perfluoroalkylation were found to completely suppress the temperature-induced fragmentation of the longer R_F chains (which leads to the unfavorable formation of "mixed" PFAFs with different R_F substituents above 300 °C in heterogeneous processes [21]). Solution-phase C_{60} perfluoroalkylation is also found to be a good method for preparation of fullerene derivatives with the highest sterically possible numbers of R_F substituents (such reactions should use a high excess of the R_FI reagent and long reaction times). Experimental results showed that many different $C_{60}(R_F)_n$ products with an "intermediate" number of substituents ($2 < n < Max(R_F/C_{60})$) are formed using the solution-phase perfluoroalkylation process. HPLC analysis of such mixtures suggests that many of these compounds can be isolated in pure state (although with a low yield). These results show that solution-phase fullerene perfluoroalkylation is a versatile technique suitable for preparation of many PFAFs with varying number of perfluorinated aliphatic or benzylic R_F groups.

Acknowledgements

This work was supported by the U. S. National Science Foundation (CHE-1012468), NIH (1R21CA140080-1A1) and the Colorado State University Research Foundation. We would like to thank the reviewers of this paper for their very thorough reading and many excellent comments that helped us to significantly improve this paper.

References

[1] A.A. Popov, I.E. Kareev, N.B. Shustova, E.B. Stukalin, S.F. Lebedkin, K. Seppelt, S.H. Strauss, O.V. Boltalina, L. Dunsch, Journal of the American Chemical Society 129 (2007) 11551–11568.
[2] A.A. Goryunkov, I.V. Kuvychko, I.N. Ioffe, D.L. Dick, L.N. Sidorov, S.H. Strauss, O.V. Boltalina, Journal of Fluorine Chemistry 124 (2003) 61–64.
[3] I.E. Kareev, I.V. Kuvychko, S.F. Lebedkin, S.M. Miller, O.P. Anderson, K. Seppelt, S.H. Strauss, O.V. Boltalina, Journal of the American Chemical Society 127 (2005) 8362–8375.
[4] I.E. Kareev, I.V. Kuvychko, S.F. Lebedkin, S.M. Miller, O.P. Anderson, S.H. Strauss, O.V. Boltalina, Chemical Communications (2006) 308–310.
[5] I.E. Kareev, N.B. Shustova, I.V. Kuvychko, S.F. Lebedkin, S.M. Miller, O.P. Anderson, A.A. Popov, S.H. Strauss, O.V. Boltalina, Journal of the American Chemical Society 128 (2006) 12268–12280.
[6] T. Mutig, E. Kemnitz, S.I. Troyanov, Journal of Fluorine Chemistry 131 (2010) 861–866.
[7] D.V. Ignat'eva, T. Mutig, A.A. Goryunkov, N.B. Tamm, E. Kemnitz, S.I. Troyanov, L.N. Sidorov, Russian Chemical Bulletin 58 (2009) 1146–1154.
[8] A.A. Popov, I.E. Kareev, N.B. Shustova, S.F. Lebedkin, S.H. Strauss, O.V. Boltalina, L. Dunsch, Chemistry – A European Journal 14 (2008) 107–121.
[9] E.I. Dorozhkin, D.V. Ignat'eva, N.B. Tamm, A.A. Goryunkov, P.A. Khavrel, I.N. Ioffe, A.A. Popov, I.V. Kuvychko, A.V. Streletskiy, V.Y. Markov, J. Spandl, S.H. Strauss, O.V. Boltalina, Chemistry – A European Journal 12 (2006) 3876–3889.
[10] N.B. Tamm, L.N. Sidorov, E. Kemnitz, S.I. Troyanov, Chemistry – A European Journal 15 (2009) 10486–10492.
[11] N.B. Tamm, L.N. Sidorov, E. Kemnitz, S.I. Troyanov, Angewandte Chemie International Edition 48 (2009) 9102–9104.
[12] I.E. Kareev, I.V. Kuvychko, N.B. Shustova, S.F. Lebedkin, V.P. Bubnov, O.P. Anderson, A.A. Popov, S.H. Strauss, O.V. Boltalina, Angewandte Chemie International Edition 47 (2008) 6204–6207.
[13] I.E. Kareev, A.A. Popov, I.V. Kuvychko, N.B. Shustova, S.F. Lebedkin, V.P. Bubnov, O.P. Anderson, K. Seppelt, S.H. Strauss, O.V. Boltalina, Journal of the American Chemical Society 130 (2008) 13471–13489.
[14] I.E. Kareev, S.F. Lebedkin, V.P. Bubnov, E.B. Yagubskii, I.N. Ioffe, P.A. Khavrel, I.V. Kuvychko, S.H. Strauss, O.V. Boltalina, Angewandte Chemie International Edition 44 (2005) 1846–1849.
[15] N.B. Shustova, D.V. Peryshkov, I.V. Kuvychko, Y.S. Chen, M.A. Mackey, C. Coumbe, D.T. Heaps, B.S. Confait, T. Heine, J.P. Phillips, S. Stevenson, L. Dunsch, A.A. Popov, S.H. Strauss, O.V. Boltalina, Journal of the American Chemical Society 133 (2010) 2672–2690.
[16] S. Yang, C. Chen, M. Jiao, N.B. Tamm, M.A. Lanskikh, E. Kemnitz, S.I. Troyanov, Inorganic Chemistry 50 (2011) 3766–3771.
[17] A.A. Popov, N.B. Shustova, A.L. Svitova, M.A. Mackey, C.E. Coumbe, J.P. Phillips, S. Stevenson, S.H. Strauss, O.V. Boltalina, L. Dunsch, Chemistry – A European Journal 16 (2010) 4721–4724.

[18] Y. Takano, M.A. Herranz, I.E. Kareev, S.H. Strauss, O.V. Boltalina, T. Akasaka, N. Martin, Journal of Organic Chemistry 74 (2009) 6902–6905.
[19] Y. Takano, M.Á. Herranz, N. Martín, G. de Miguel Rojas, D.M. Guldi, I.E. Kareev, S.H. Strauss, O.V. Boltalina, T. Tsuchiya, T. Akasaka, Chemistry – A European Journal 16 (2010) 5343–5353.
[20] A.G. Avent, O.V. Boltalina, A.V. Goryunkov, A.D. Darwish, V.Y. Markov, R. Taylor, Fullerenes, Nanotubes, and Carbon Nanostructures 10 (2002) 235–241.
[21] N.B. Shustova, I.E. Kareev, I.V. Kuvychko, J.B. Whitaker, S.F. Lebedkin, A.A. Popov, Y.S. Chen, K. Seppelt, S.H. Strauss, O.V. Boltalina, Journal of Fluorine Chemistry 131 (2010) 1198–1212.
[22] I.V. Kuvychko, J.B. Whitaker, B.W. Larson, R.S. Raguindin, K.J. Suhr, S.H. Strauss, O.V. Boltalina, Journal of Fluorine Chemistry 132 (2011) 679–685.
[23] I.V. Kuvychko, J.W. Whitaker, B.W. Larson, T.C. Folsom, N.B. Shustova, S.M. Avdoshenko, Y.-S. Chen, H. Wen, X.-B. Wang, L. Dunsch, A.A. Popov, O.V. Boltalina, S.H. Strauss, Chemical Science (2012), http://dx.doi.org/10.1039/C2SC01133F (advance article).
[24] N.B. Shustova, I.V. Kuvychko, D.V. Peryshkov, J.B. Whitaker, B.W. Larson, Y.S. Chen, L. Dunsch, K. Seppelt, A.A.H.S.S. Popov, O.V. Boltalina, Chemical Communications 47 (2010) 875–877.
[25] O.V. Boltalina, A.Y. Lukonin, J.M. Street, R. Taylor, Chemical Communications (2000) 1601–1602.
[26] I.V. Kuvychko, A.A. Streletskii, N.B. Shustova, K. Seppelt, T. Drewello, A.A. Popov, S.H. Strauss, O.V. Boltalina, Journal of the American Chemical Society 132 (2010) 6443–6462.
[27] E.I. Dorozhkin, A.A. Goryunkov, I.N. Ioffe, S.M. Avdoshenko, V.Y. Markov, N.B. Tamm, D.V. Ignat'eva, L.N. Sidorov, S.I. Troyanov, European Journal of Organic Chemistry (2007) 5082–5094.
[28] P.J. Krusic, E. Wasserman, B.A. Parkinson, B. Malone, E.R. Holler, Journal of the American Chemical Society 113 (1991) 6274–6275.
[29] P.J. Fagan, P.J. Krusic, C.N. McEwen, J. Lazar, D.H. Parker, N. Herron, E. Wasserman, Science 262 (1993) 404–407.
[30] R. Borghi, L. Lunazzi, G. Placucci, P.J. Krusic, D.A. Dixon, J.L.B. Knight, Journal of Physical Chemistry 98 (1994) 5395–5398.
[31] R. Borghi, L. Lunazzi, G. Placucci, P.J. Krusic, D.A. Dixon, N. Matsuzawa, M. Ata, Journal of the American Chemical Society 118 (1996) 7608–7617.
[32] J.R. Morton, K.F. Preston, Journal of Physical Chemistry 98 (1994) 4993–4997.
[33] J.R. Morton, F. Negri, K.F. Preston, G. Ruel, Journal of Physical Chemistry 99 (1995) 10114–10117.
[34] M. Yoshida, Y. Morinaga, M. Iyoda, K. Kikuchi, I. Ikemoto, Y. Achiba, Tetrahedron Letters 34 (1993) 7629–7632.
[35] M. Yoshida, A. Morishima, Y. Morinaga, M. Iyoda, Tetrahedron Letters 35 (1994) 9045–9046.
[36] M. Yoshida, F. Sultana, N. Uchiyama, Y. Yamada, M. Iyoda, Tetrahedron Letters 40 (1999) 735–736.
[37] W. Chen, T.J. McCarthy, Macromolecules 32 (1999) 2342–2347.
[38] Y.Y. Duan, L. Shi, L.Q. Sun, M.S. Zhu, L.Z. Han, International Journal of Thermophysics 21 (2000) 393–404.
[39] R.J. Doome, S. Dermaut, A. Fonseca, M. Hammida, J.B. Nagy, Fullerenes, Nanotubes, and Carbon Nanostructures 5 (1997) 1593–1606.
[40] R. Doome, A. Fonseca, J.B. Nagy, Molecular Materials 13 (2000) 201–208.
[41] J.W.R. Dolbier, Chemical Reviews 96 (1996) 1557–1584.
[42] A.B. Cowell, C. Tamborski, Journal of Fluorine Chemistry 17 (1981) 345–356.
[43] H. Sawada, M. Nakayama, Journal of Fluorine Chemistry 51 (1991) 117–129.
[44] A. Bravo, H.-R. Bjørsvik, F. Fontana, L. Liguori, A. Mele, F. Minisci, Journal of Organic Chemistry 62 (1997) 7128–7136.
[45] F. Antonietti, C. Gambarotti, A. Mele, F. Minisci, R. Paganelli, C. Punta, F. Recupero, European Journal of Organic Chemistry (2005) 4434–4440.
[46] Y. Li, C. Li, W. Yue, W. Jiang, R. Kopecek, J. Qu, Z. Wang, Organic Letters 12 (2010) 2374–2377.
[47] Q.-L. Zhou, Y.-Z. Huang, Journal of Fluorine Chemistry 43 (1989) 385–392.
[48] R.N. Loy, M.S. Sandford, Organic Letters 13 (2011) 2548–2551.
[49] D.V. Avila, K.U. Ingold, J. Lusztyk, W.R. Dolbier, H.Q. Pan, Journal of the American Chemical Society 115 (1993) 1577–1579.
[50] D.V. Avila, K.U. Ingold, J. Lusztyk, W.R. Dolbier, H.Q. Pan, M. Muir, Journal of the American Chemical Society 116 (1994) 99–104.
[51] F. Antonietti, A. Mele, F. Minisci, C. Punta, F. Recupero, F. Fontana, Journal of Fluorine Chemistry 125 (2004) 205–211.
[52] R.S. Ruoff, D.S. Tse, R. Malhotra, D.C. Lorents, Journal of Physical Chemistry 97 (1993) 3379–3383.
[53] A. Hirsch, M. Brettreich, Fullerenes – Chemistry and Reactions, Wiley-VCH, Weinheim, 2005, p. 221.
[54] R.D. Chambers, Fluorine in Organic Chemistry, Blackwell Publishing Ltd., 2004.
[55] N. Krause, Modern Organocopper Chemistry, Wiley-VCH Verlag GmbH, 2002.
[56] O.A. Tomashenko, V.V. Grushin, Chemical Reviews 111 (2011) 4475–4521.
[57] I.S. Uzkikh, E.I. Dorozhkin, O.V. Boltalina, A.I. Boltalin, Doklady Akademii Nauk 379 (2001) 344–347.