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Pressure effect on heterogeneous trifluoromethylation of fullerenes and its application

Igor V. Kuvychko [a,*], James B. Whitaker [a], Bryon W. Larson [a], Rachel S. Raguindin [a,b], Kristin J. Suhr [a], Steven H. Strauss [a,*], Olga V. Boltalina [a,*]

[a] Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA
[b] REU student at CSU from Adams State College, CO, USA

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Dedicated to Alain Tressaud
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the ACS Award for Creative
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ABSTRACT

The first systematic study of heterogeneous fullerene trifluoromethylation using an innovative gradient-temperature gas–solid reactor revealed a significant effect of CF_3I pressure on the conversion of C_{60} and C_{70} into trifluoromethylated products and on the range of fullerene$(CF_3)_n$ compositions that were obtained. The design of the reactor allowed us to lower the residence times of fullerene$(CF_3)_n$ species in the hot zone which resulted in the significant differences in relative isomeric distributions as compared to the earlier methods. For the first time, gram quantities of trifluoromethylated fullerenes were prepared using the new reactor, and the selective synthesis of a single-isomer $C_{60}(CF_3)_2$ was developed. The relative reactivity of C_{70} as a CF_3 radical scavenger was found to be much lower than that of C_{60}, especially at an early radical addition stage, which led to the cost-efficient synthesis of $C_{60}(CF_3)_2$ from a fullerene extract.

1. Introduction

Poly(perfluoroalkyl)fullerenes (PFAFs) constitute a unique class of fullerene derivatives due to the combination of their high thermal stabilities [1], exceptionally long lifetimes of their radical anions in solution [2,3], and a broad range (0.8 V) of the first reduction potentials that strongly depend on the number of substituents, their nature, and especially their addition pattern [4]. These properties make PFAFs promising materials for electrochemical and photoelectrochemical applications where a proper match between HOMO/LUMO levels of different molecular components is paramount for the optimal performance. Currently, the most populous and best-studied class of PFAFs is represented by trifluoromethylated derivatives (fullerene$(CF_3)_n$ or TMFs) of C_{60} and C_{70} [1,3,5–7], various higher fullerenes [8], including endometallofullerenes [9], and metallic nitride fullerenes [10]. Fullerene$(CF_3)_n$ with n ranging from two [5] to eighteen [11] have been isolated and studied by a wide array of spectroscopic, structural, and electrochemical [2,3] methods, but further advances in applications of these compounds critically depend on their availability in practical amounts. Currently, almost all isomerically pure TMFs have been isolated in few-mg amounts by high performance liquid chromatography (HPLC) from complex crude mixtures (the only exception is C_1–$C_{70}(CF_3)_{10}$ [3,12] that can be prepared with high yield in 100+ mg batches). The synthesis of TMFs relies on high-temperature reactions between a fullerene substrate and CF_3 radical precursors ($AgOOCCF_3$ or CF_3I) [7,13–15]. These methods generally produce TMF mixtures of a particular composition which is difficult to adjust (each method is best suited for a preparation of a particular range of TMF compositions with a certain isomeric distribution; e.g., “low” TMFs with 2–4 CF_3 groups per fullerene cage can only be produced in trace amounts). Furthermore, these methods have low efficiencies and are difficult

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* Corresponding authors. Tel.: +1 970 491 5088; fax: +1 970 491 1801.
E-mail addresses: igor.kuvychko@gmail.com (I.V. Kuvychko), jamesbwhitaker@gmail.com (J.B. Whitaker), bwlarson@gmail.com (B.W. Larson), santosraguindinra@grizzlies.adams.edu (R.S. Raguindin), kjs21sammy@aol.com (K.J. Suhr), steven.strauss@colostate.edu (S.H. Strauss), olga.boltalina@colostate.edu (O.V. Boltalina).

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to scale up (the preparation of larger quantities of TMFs for practical studies and/or applications is prohibitively difficult) [5,7,13–17]. In this work we use a novel reactor to perform the first systematic study of the effects of reaction parameters on a heterogeneous fullerene trifluoromethylation; the results allowed us to largely solve the aforementioned problems.

2. Results and discussion

2.1. Fullerene trifluoromethylation: general remarks

A thermally-induced heterogeneous reaction between a solid fullerene and a gaseous CF_3I reagent is a complex process that is likely to involve several elementary steps depicted in Scheme 1. The elementary processes that occur during fullerene trifluoromethylation are: (i) thermolysis of CF_3I producing CF_3 radicals; (ii) sublimation of C_{60} from the hot zone; (iii) trifluoromethylation of the surface layer of the solid C_{60} (and further trifluoromethylation of so-formed solid TMFs) in the hot zone; (iv) sublimation of TMFs from the hot zone; (v) trifluoromethylation of the subliming C_{60} and TMFs in the gas phase; and vi) condensation of C_{60} and TMFs from the gas phase into the cold zone. Trifluoromethylation of fullerenes is treated as an irreversible process; it is also assumed that the sublimation of fullerenes and TMFs out of the cold zone does not take place. The composition of the TMF products depends on the concentration of CF_3 radicals and the residence time of fullerene species in the hot zone (the time that a fullerene molecule spends in the volume where the probability of the reaction with CF_3 radical(s) is high). It is clear that various experimental factors that increase the concentration of CF_3 radicals and/or residence times (of the fullerene species) should (i) favour the formation of fullerene$(CF_3)_{n>6}$, (referred to as "higher TMFs") and (ii) improve fullerene conversion. These experimental factors include (i) CF_3I pressure, (ii) temperature of the hot zone (T_{hz}), (iii) size of the hot zone (L_{hz}), (iv) gas composition and (v) presence of a promoter (copper powder, see below).

2.2. Effects of the reaction parameters on C_{60} trifluoromethylation

Effects of the reaction parameters on C_{60} trifluoromethylation were explored using a specialized gradient-temperature gas–solid (GTGS) reactor shown in Fig. 1 (see also Figs. S-1 and S-2). The design enabled the following unique capabilities: (i) a static regime (constant $P(CF_3I) = 0.5–800$ torr) and a flow regime ($P(CF_3I)$ = atmospheric pressure) operation; (ii) use of gas mixures; (iii) variable size of the hot zone (2–50 mm). In a typical experiment, 3.9–4.9 mg of a finely ground C_{60} were reacted with CF_3I under various conditions, see Table 1 (see also Table S-1). Each entry listed in Table 1 corresponds to an array of experiments carried out under different CF_3I pressures (5, 15, 30, 45, 135 torr, and also 410 torr for experiments A and B). Each crude product was analyzed by high performance liquid chromatography (HPLC) and the resulting sets of HPLC traces were stacked into 3D waterfall plots, see Fig. 2 (see also Supporting Information [SI] for the details of sampling and trace normalization). The compositional distribution of TMFs in the crude products was also studied using atmospheric pressure chemical ionization mass spectrometry (APCI-MS) in the negative-ion mode. The results of the APCI mass spectrometry were validated using a standard solution containing both $C_{60}(CF_3)_2$ and $C_{60}(CF_3)_{10}$ (isomer 3) in 100/61 molar ratio. Little to no fragmentation was observed; the intensity ratio of $C_{60}(CF_3)_2^-$ and $C_{60}(CF_3)_{10}^-$ peaks was found to be 100/75, indicating little discrimination (or suppression effect, see Fig. S-3). The identification of the HPLC peaks in the traces of crude TMF mixtures was accomplished by their HPLC separation followed by their analysis using APCI mass spectrometry, ^{19}F NMR and UV–vis spectroscopy. In agreement with earlier results [4,5], the relative retention times of fullerene$(CF_3)_n$ generally were inversely proportional to the n value. Multiple repetitions of individual experiments were performed, which demonstrated a good reproducibility (see Fig. S-4).

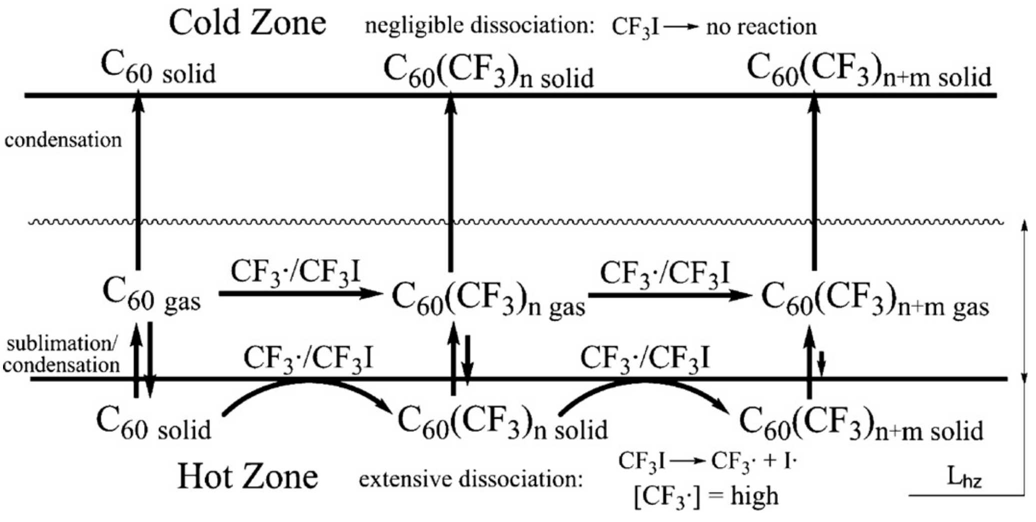
Table 1
Reaction conditions for C_{60} and C_{70} trifluoromethylation in the GTGS reactor (each experiment was repeated under different pressures of CF_3I).

Experiment	Substrate	T_{hz}[a] (°C)	L_{spacer} (mm)	Reaction time (min)
A	C_{60}	480	10	30
B	C_{60}	480	10	90
C	C_{60}	450	10	30
D	C_{60}	530	10	30
E	C_{60}	480	50	30
F[b]	C_{60}	460	10	30
G[c]	C_{60}	410	10	30
H	C_{70}	480	10	30
K	C_{70}	530	10	90
L[c]	C_{70}	410	10	30

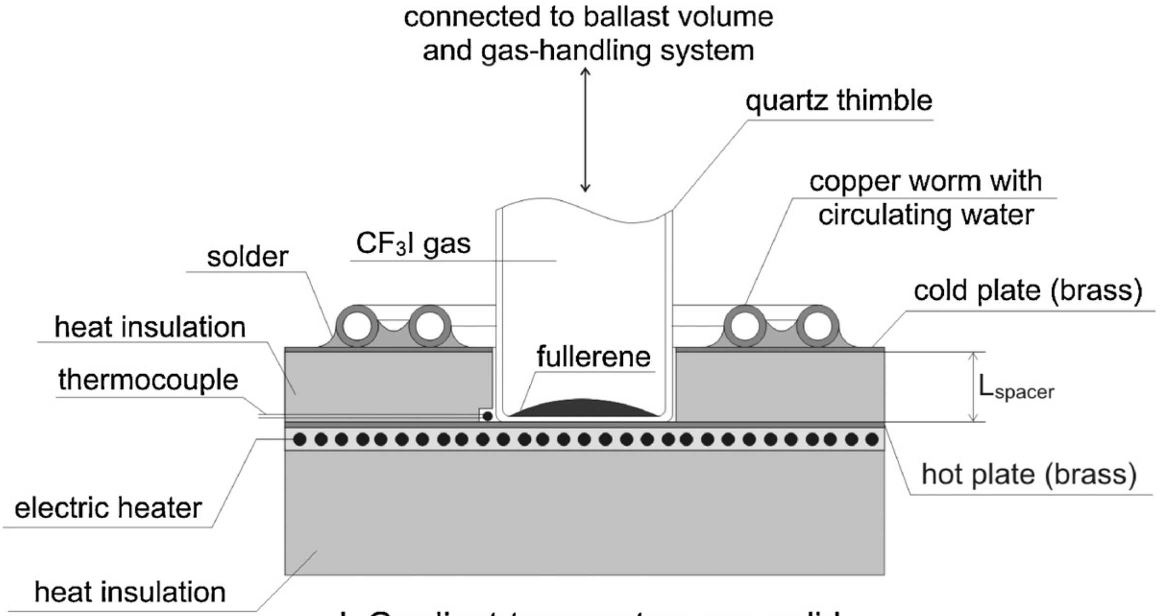
[a] See Table S-1 and the corresponding footnotes for a detailed discussion of the temperature measurements.

[b] Cold finger was used (ca. 5 mm distance between fullerene sample in the hot zone and the tip of the cold finger was maintained).

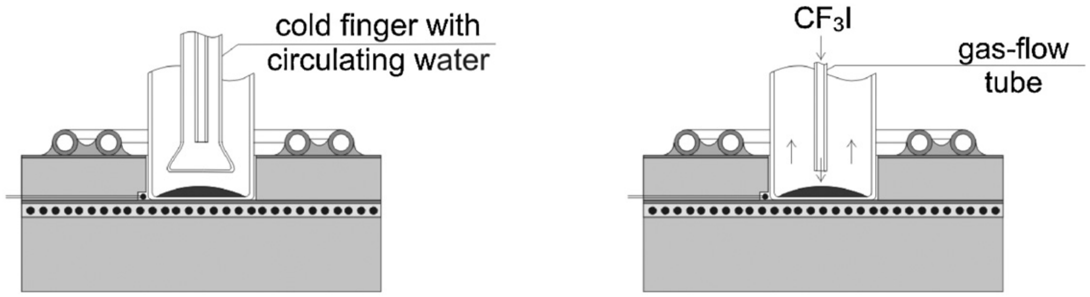
[c] Copper powder (ca. 400 mg) was mixed with fullerene substrate.



Scheme 1.



I. Gradient-temperature gas-solid (GTGS) reactor (basic configuration)



II. Reactor equipped with a cold finger

III. Reactor equipped with a flow tube

Fig. 1. Basic configuration of the gradient-temperature gas–solid (GTGS) reactor (I); GTGS reactor equipped with an internal water-cooled cold finger (II); GTGS reactor equipped with an internal gas-injection tube for experiments with CF_3I flow (III).

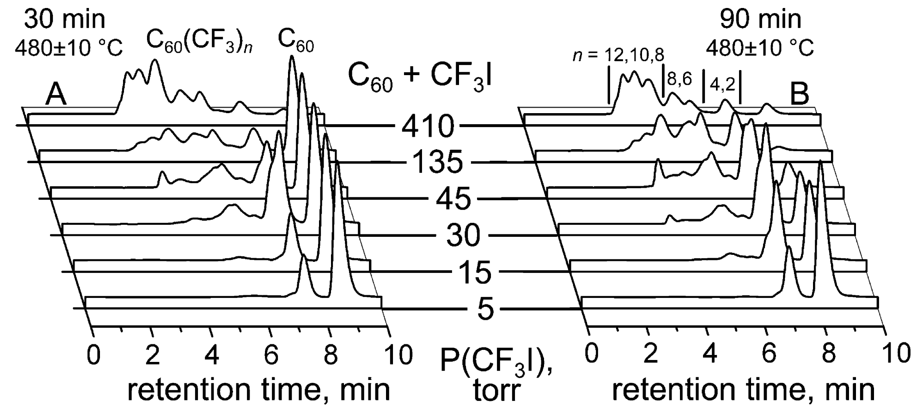


Fig. 2. Waterfall plots of the normalized HPLC traces of the products of C_{60} trifluoromethylation in the GTGS reactor under different pressures of CF_3I. Experiments A and B were performed under identical reaction conditions (see Table 1) except for the reaction time (30 min for experiments A and 90 min for experiments B). Neat toluene eluent at 5 mL min^{-1} flow rate was used for the HPLC analysis.

2.2.1. CF_3I pressure

Trifluoromethylation of C_{60} under 5 and 15 torr of CF_3I produced ca. 80–90% pure $C_{60}(CF_3)_2$; the use of 30–45 torr of CF_3I led to the formation of mixtures of $C_{60}(CF_3)_{2,4}$, see Fig. 2A and Table 1. A Further increase of the reaction pressure to 135–410 torr shifted the TMF distribution to $C_{60}(CF_3)_{6,8,10}$ (see Fig. S-5). A higher pressure of CF_3I was likely to increase the concentration of CF_3 radicals and at the same time suppress the sublimation of fullerenes from the hot zone leading to longer residence times; both effects led to the formation of TMFs with higher *n* values. A low probability of the reaction between CF_3 radicals and C_{60} under 5–10 torr of CF_3I led to a selective formation of $C_{60}(CF_3)_2$ (achieved at a trade-off for low fullerene conversion – a "low conversion" regime).

2.2.2. Reaction time

Two sets of experiments A and B were carried out for 30 and 90 min correspondingly, see Fig. 2 (all other parameters were kept the same; see Table 1). Longer reaction time significantly improved the conversion of C_{60}; it also slightly shifted the product distribution to higher TMFs. The latter change indicated that the transport of the TMFs from the hot zone is relatively slow; some of the TMFs formed during the first 30 min of the reaction remained within the hot zone and were subsequently converted into higher TMF species. It was also confirmed by the analysis of the sublimed products collected in the cold zone and the solid residue that remained in the hot zone. The analysis showed that TMFs were indeed present in the hot-zone residues; the sublimate, on the other hand, contained unreacted C_{60} (the sublimates formed in the 135–410 torr experiments did not contain any C_{60}). These observations are in agreement with the Scheme 1: (i) a sublimation of TMFs and unreacted fullerene from the hot zone does take place, and (ii) the presence of TMFs in the solid residue within the hot zone strongly suggests that fullerene trifluoromethylation takes place on the surface of the solid fullerene/TMF particles (a significant re-condensation of TMFs within the volume of the hot zone is unlikely).

2.2.3. Reaction temperature

Three sets of experiments C, A, and D were performed under T_{hz} = 450, 480 and 530 °C, see Fig. 3 (top row; see also Fig. S-6). The conversion increased at a higher reaction temperature, in accord with a higher concentration of CF_3 radicals (under all studied pressures of CF_3I; C_{60} trifluoromethylation became extremely slow at $T_{hz} < 440$ °C). The changes of the TMF compositions depended on the CF_3I pressure. For the reactions carried out under $P(CF_3I)$ = 45 torr the composition of TMF products shifted towards higher TMFs at a *lower* temperature, see Figs. 4 and S-7; under $P(CF_3I)$ = 135 torr the composition shifted towards higher TMFs at a *higher* temperatures, cf. Figs. 4, S-7 and S-8.

These observations can be explained as follows: a higher temperature leads to an increase in the concentration of CF_3 radicals (favoring higher TMFs) but it also increases the sublimation rate thereby decreasing the residence time (favoring lower TMFs). This competition between two opposing factors makes the net effect of the reaction temperature on the TMF composition difficult to predict (a final optimization of a particular TMF synthesis requires an experimental survey of a temperature range).

2.2.4. Size of the hot zone

Three sets of experiments differing by the size of the reactor hot zone were carried out: (i) experiment E with L_{spacer} = 50 mm; (ii) experiment A with L_{spacer} = 10 mm; (iii) experiment F with L_{spacer} = 10 mm and a cold finger installed in a close proximity to the hot zone (see Table 1 and Figs. 3 and 4). The larger hot zone of experiment E led to a significantly higher C_{60} conversion; the smaller hot zone of the experiment F led to a lower C_{60} conversion. The larger hot zone also shifted the product distribution towards higher TMFs (see Figs. S-7 and S-9). These effects are fully consistent with a change of the residence time with the size of the hot zone.

Comparison of the relative distributions of $C_{60}(CF_3)_n$ isomers (for *n* = 6–10) in the TMFs prepared in the GTGS reactor and a conventional flow-tube reactor under identical temperature and CF_3I pressure showed that trifluoromethylation in the GTGS

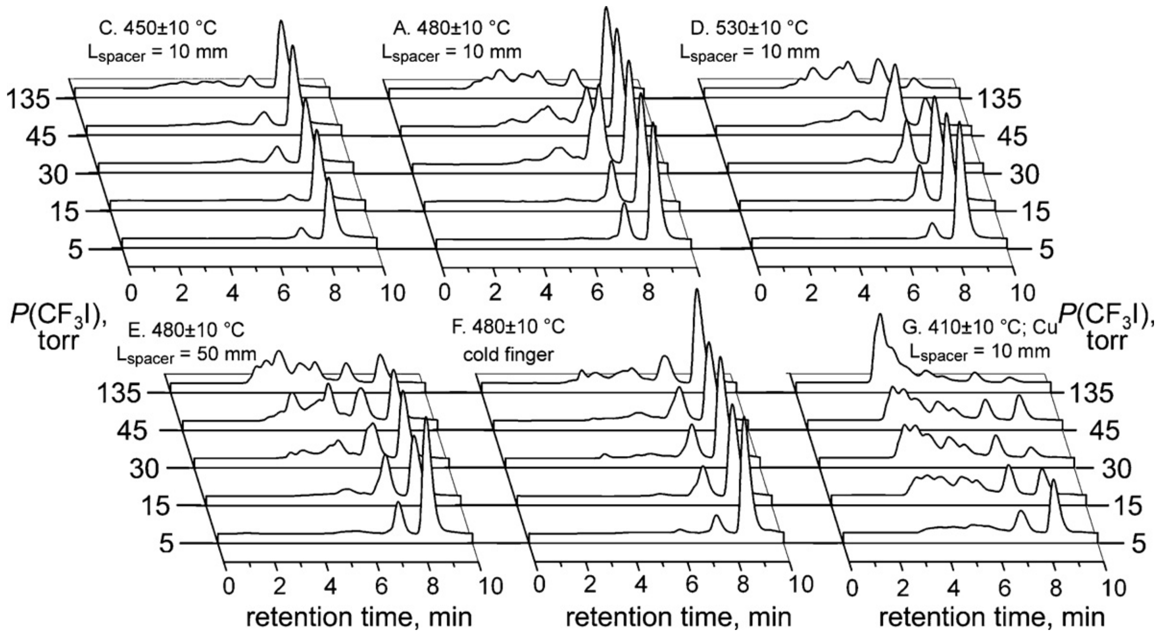


Fig. 3. Waterfall plots of the normalized HPLC traces of the products of C_{60} trifluoromethylation in the GTGS reactor under different conditions (see Table 1). Neat toluene eluent at 5 mL min^{-1} flow rate was used for the HPLC analysis.

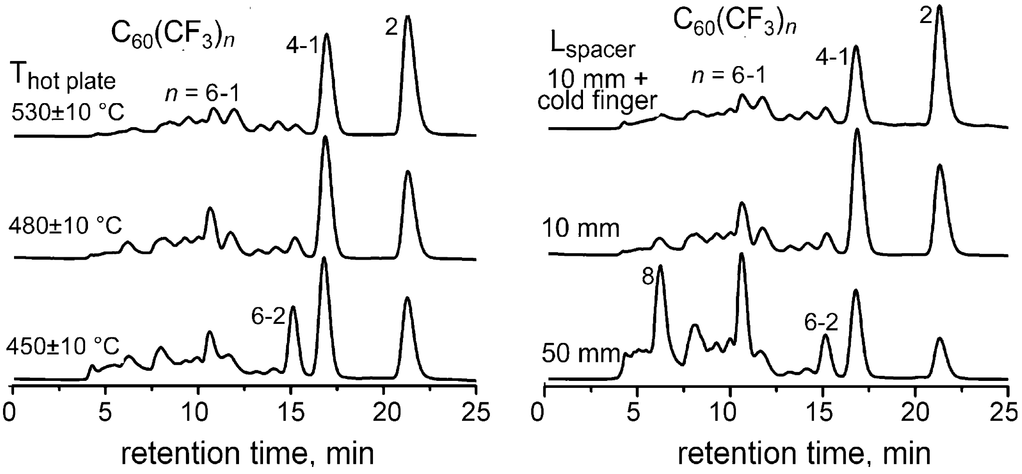


Fig. 4. HPLC analysis of the C_{60} trifluoromethylation products prepared in the GTGS reactor using 45 torr of CF_3I. Left column corresponds to the products formed in the experiments C, A, and D (from bottom to top); right column corresponds the products formed in the experiment E, A, and F (from bottom to top). A mixture of 70/30 v/v toluene/acetonitrile at 5 mL min^{-1} flow rate was used as the eluent for the HPLC analysis.

reactor produced many new TMFs as compared to a flow-tube reactor (see Fig. 5). The residence time of TMFs in the flow-tube reactor is much longer than in the GTGS reactor; this enables the formation of fewer more stable isomers due to annealing. For example, the six most abundant isomers of $C_{60}(CF_3)_{10}$ that were isolated from the crude material prepared in the flow-tube reactor constitute the top six most stable isomers, with a small energy gap of 10 kJ/mol, according to the DFT calculations [4]. In contrast, the crude product from the GTGS-reactor synthesis produced many more isomers of $C_{60}(CF_3)_{10}$ with fairly even relative abundances, as follows from the comparison of the HPLC traces. Therefore, the use of the new GTGS reactor makes it possible to prepare many more new isomers of TMFs with unknown addition patterns and, as a consequence, different physicochemical properties. (See sections below and Supporting Information "Selectivity of fullerene trifluoromethylation" for further discussion.)

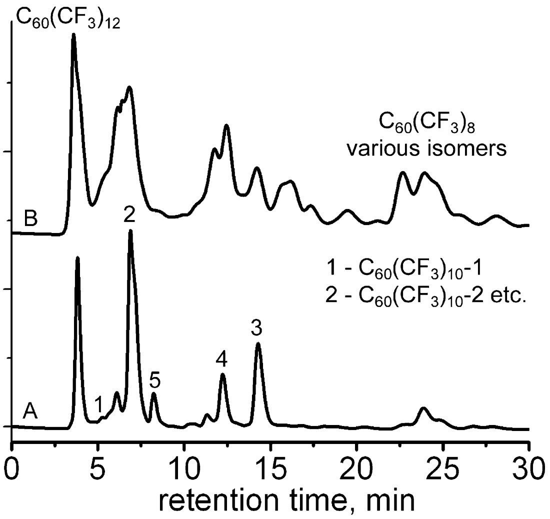


Fig. 5. Expansions of HPLC traces of two TMF mixtures prepared by trifluoromethylation of C_{60} sample with 640 torr of CF_3I in the GTGS reactor (top trace, T_{hz} = 480 °C) and in the flow-tube reactor (bottom trace, T_{hz} = 480 °C); 20/80 v/v toluene/heptanes eluent at 5 mL/min flow rate was used for the analysis.

2.2.5. Effects of inert buffer gas and copper metal

The introduction of an inert buffer gas (15 torr of N_2 added to the 15 torr of CF_3I) led to a drastic decrease of fullerene conversion; only a very small amount of $C_{60}(CF_3)_2$ was formed (less than 1% yield). This direction was not pursued further because of the low fullerene conversion.

Copper powder is commonly used to facilitate the dissociation of perfluoroalkyl iodides and scavenge iodine (it was used for a preparation of some fullerene$(C_2F_5)_n$) [18–20]. In this study, the effect of copper metal on the trifluoromethylation of C_{60} with CF_3I was evaluated. The control experiments showed that in the presence of copper powder (either with or without C_{60} present) CF_3I decomposition took place at a significantly lower temperature (T_{hz} = 320 °C vs. 450 °C without Cu; $P(CF_3I)$ = 45 torr). The thermolysis of CF_3I was detected by a visible formation of CuI or I_2 vapour (all elemental iodine was scavenged in the presence of copper due to the formation of CuI). The trifluoromethylation of C_{60} in the presence of copper readily took place at a very low temperature of T_{hz} = 410 °C, and a high conversion of C_{60} was achieved (see Fig. 3, experiment G). In contrast, a control experiment carried out under identical conditions but without copper showed no signs of C_{60} trifluoromethylation (see SI for the further discussion on temperature effects). The use of copper also shifted the product composition towards higher TMFs with n values up to 14 (Fig. S-10; no $C_{60}(CF_3)_{n>10}$ were observed in the analogous reactions carried out without copper). These effects are likely to be due to a high concentration of CF_3 radicals generated in the presence of copper combined with low rates of C_{60} and TMF sublimation from the hot zone due to low reaction temperatures.

2.3. Selective synthesis of $C_{60}(CF_3)_2$

Previous studies of polyadditions of halogen-containing radicals to fullerenes demonstrated that selective syntheses of the simplest derivatives, the bis-adducts, are very difficult, if not impossible, to achieve. For example, in fluorination and chlorination of C_{60}, single isomers of $C_{60}F_2$ [21] and $C_{60}Cl_2$ [22] were only formed as minor impurities; $C_{60}Br_2$ has never been observed experimentally. Perfluoroalkylation reactions have been known to produce derivatives with high degree of addition very easily, whereas bis-adducts were formed as minor products. In this work, optimal conditions for the selective synthesis of $C_{60}(CF_3)_2$ were found for the first time; this compound, a potentially valuable synthon, was prepared for the

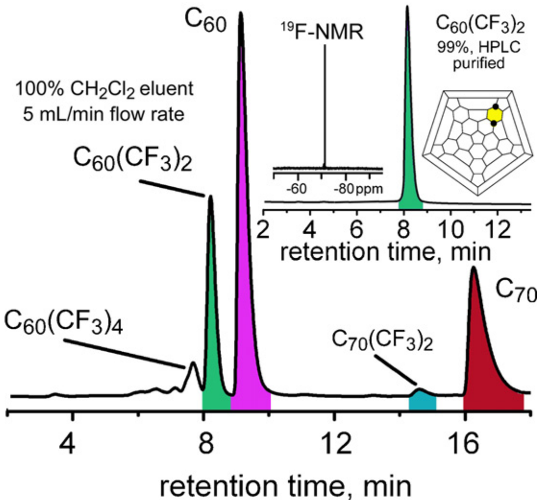


Fig. 6. HPLC analysis of the crude product obtained from 120 mg of fullerene extract in the GTGS reactor (10 torr of CF_3I, T_{hz} = 480 °C, L_{spacer} = 10 mm, cold finger used to capture the iodine). Pure $C_{60}(CF_3)_2$ was isolated from the crude using HPLC and analyzed by ^{19}F NMR spectrscopy and HPLC, see inserts.

first time in multi-hundred-mg amounts with 20–25% molar yield based on starting C_{60}, see Fig. 6. It is also notable that when a crude fullerene extract was used as a starting material no decrease in the yield or the purity of $C_{60}(CF_3)_2$ was observed. During the scaleup of this reaction it was found that iodine had to be removed from the reaction zone in order to maintain a high conversion (see Fig. S-11); a cold finger condenser positioned 20 mm above the fullerene sample was used as a very efficient iodine trap. Large-scale reactions were also performed at higher CF_3I pressures (15 and 45 torr) using pure C_{60} as a starting material, and these yielded 100+ mg amounts of $C_{60}(CF_3)_{4,6}$.

2.4. Trifluoromethylation of C_{70}

Trifluoromethylation of C_{70} was studied analogously to the trifluoromethylation of C_{60}. Three experiments H, K, and L were performed in order to ascertain the effects of CF_3I pressure (5−410 torr), temperature (T_{hz} = 410, 480, and 530 °C), and the presence of copper metal on the $C_{70}(CF_3)_n$ composition and C_{70} conversion, see Table 1 and Fig. 7. Similar to the case of C_{60}, the pressure of CF_3I has a very strong effect on the composition of the TMF products. The use of low pressures of CF_3I (5–45 torr) leads to mixtures of $C_{70}(CF_3)_{2,4,6}$ with very low yields, see Fig. S-12. As the pressure was increased to 135 and then to 410 torr, the product composition shifted to $C_{70}(CF_3)_{8,10}$; the C_{70} conversion increased drastically to ca. 90%. A low-conversion regime of C_{70} trifluoromethylation did produce $C_{70}(CF_3)_2$ selectively (similar to C_{60}) but the yield was too low to be practical (1% vs. 20–30% for the C_{60} trifluoromethylation). These results show that C_{70} has a much lower reactivity as compared to C_{60} under identical reaction conditions. This experimental observation lies in excellent agreement with the calculated enthalpies of the isodesmic reactions of fullerenes and TMFs with $C_{60}(CF_3)_2$ [23]. For example, ΔH(1) = 7.2 kJ/mol which indicates that C_{70} trifluoromethylation is a less energetically favourable process than that of C_{60}.

$$C_{70} + C_{60}(CF_3)_2 \rightarrow C_{70}(CF_3)_2 + C_{60} \qquad (1)$$

Due to a lower reactivity of C_{70} at the early addition stages, it was possible to use a crude fullerene extract as a starting material for the efficient synthesis of $C_{60}(CF_3)_2$, see above. The presence of copper powder in the hot zone led to a greater conversion of C_{70} (even at T_{hz} = 410 °C); no trifluoromethylation of C_{70} was observed under these conditions without copper. The presence of copper also shifted the composition of TMFs to higher n values compared to the reactions without copper: at low pressures of CF_3I (5–45 torr) main products were $C_{70}(CF_3)_{8,10}$; at a higher pressure of CF_3I (135 torr) TMFs containing up to sixteen CF_3 groups were formed (see Fig. S-13). A more detailed analysis of the distribution of isomers of $C_{70}(CF_3)_n$ revealed that many more isomers for n = 8,10 were formed than in the products obtained in flow-tube reactors [1] or in sealed ampoules; [11] this indicates that some thermally-induced equilibration of the TMF isomers may be taking place in longer hot zones (at longer residence times). Currently, the work on the isolation and characterization of new $C_{70}(CF_3)_n$ isomers is under way.

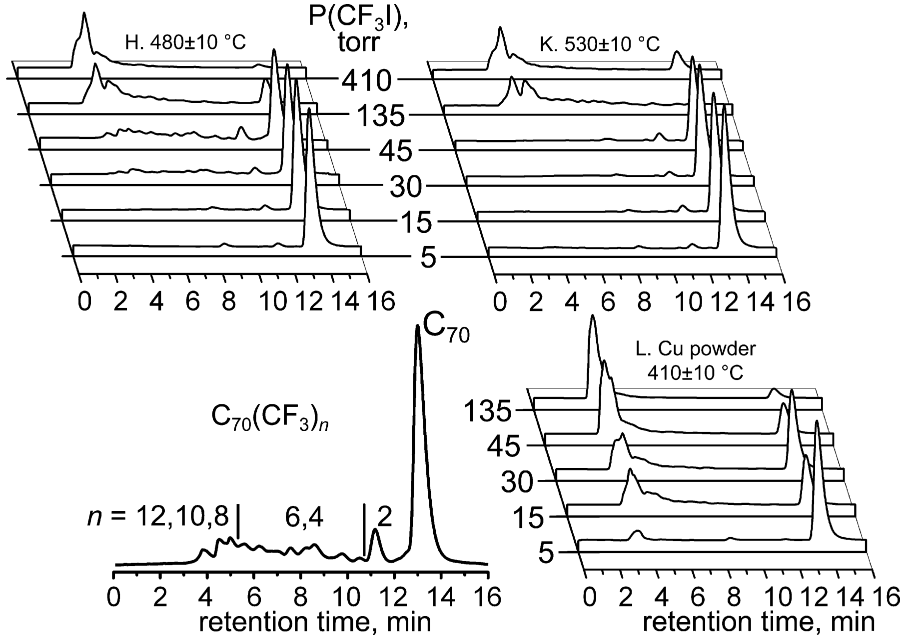


Fig. 7. Waterfall plots of the normalized HPLC traces of the products of C_{70} trifluoromethylation in GTGS reactor, see Table 1. The HPLC trace in the lower left corner of the figure. corresponds to the product prepared at 45 torr of CF_3I at T_{hz} = 480 °C (experiment H).

3. Conclusions

The first systematic study of the heterogeneous high-temperature fullerene trifluoromethylation revealed that the fullerene conversion and the composition of the TMF products can be controlled in a wide range by the pressure of CF_3I and, to a lesser extent, by other reaction conditions such as temperature, size of the hot zone, and the presence or absence of a copper metal. These data led to the preparation of multi-hundred-mg quantities of TMFs of various compositions. This work also demonstrated that not all fullerenes can be viewed as radical "sponges", i.e., molecules that have very low activation energy barriers for radical addition reactions (the rate of trifluoromethylation of C_{70} was found to be much lower as compared to C_{60}; due to this difference it was possible to realize a selective synthesis of $C_{60}(CF_3)_2$ from inexpensive fullerene extract). These new developments provide a further advancement in the large-scale synthesis and physicochemical characterization of the robust fullerene$(CF_3)_n$ acceptors with highly tunable electrochemical properties. Finally, the new GTGS reactor can be adopted by synthetic chemists interested in studies of various heterogeneous gas/solid reactions.

4. Materials and methods

4.1. Reagents and solvents

HPLC Grade toluene, heptanes (Fisher Scientific), and CH_2Cl_2 (Fisher Scientific) were used as received. C_{60} (99.9%, Term-USA), CF_3I, (SynQuest Labs), and copper powder (Fischer Scientific) were used as received.

4.2. Instruments

HPLC analysis and separation was done using a Shimadzu liquid chromatography instrument (CBM-20A control module, SPD-20A UV-detector set to 300 nm detection wavelength, LC-6AD pump, manual injector valve) equipped with a 10-mm I.D. × 250 mm Cosmosil Buckyprep column, Nacalai Tesque, Inc.). APCI mass spectra were recorded on a 2000 Finnigan LCQ-DUO mass-spectrometer (CH_3CN carrier solvent, 0.3 mL min^{-1} flow rate, TMF sample injected as solution in toluene). For a detailed description of the GTGS reactor and a typical experiment see Supporting Information.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2011.03.008.

References

[1] I.E. Kareev, I.V. Kuvychko, S.F. Lebedkin, S.M. Miller, O.P. Anderson, K. Seppelt, S.H. Strauss, O.B. Boltalina, J. Am. Chem. Soc. 127 (2005) 8362–8375.

[2] A.A. Popov, J. Tarabek, I.E. Kareev, S.F. Lebedkin, S.H. Strauss, O.B. Boltalina, L. Dunsch, J. Phys. Chem. A 109 (2005) 9709–9711.

[3] A.A. Popov, I.E. Kareev, N.B. Shustova, S.F. Lebedkin, S.H. Strauss, O.B. Boltalina, L. Dunsch, Chem. Eur. J. 14 (2008) 107–121.

[4] A.A. Popov, I.E. Kareev, N.B. Shustova, E.B. Stukalin, S.F. Lebedkin, K. Seppelt, S.H. Strauss, O.B. Boltalina, L. Dunsch, J. Am. Chem. Soc. 129 (2007) 11551–11568.

[5] A.A. Goryunkov, I.V. Kuvychko, I.N. Ioffe, D.L. Dick, L.N. Sidorov, S.H. Strauss, O.B. Boltalina, J. Fluorine Chem. 124 (2003) 61–64.

[6] A.A. Goryunkov, I.N. Ioffe, I.V. Kuvychko, T.S. Yankova, V.Y. Markov, A.A. Streletskii, D.L. Dick, L.N. Sidorov, O.B. Boltalina, S.H. Strauss, Fullerenes Nanotubes Carbon Nanostr. 12 (2004) 181–185.

[7] S.I. Troyanov, A. Dimitrov, E. Kemnitz, Angew. Chem. Int. Ed. 45 (2006) 1971–1974.

[8] N.B. Tamm, S.M. Avdoshenko, E. Kemnitz, S.I. Troyanov, Russ. Chem. Bull. 56 (2007) 915–921.

[9] 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, Angew. Chem. Int. Ed. 44 (2005) 1846–1849.

[10] N.B. Shustova, A.A. Popov, M.A. Mackey, C.E.J. Coumbe, P. Phillips, S. Stevenson, S.H. Strauss, O.V. Boltalina, J. Am. Ceram. Soc. 129 (2007) 11676–11677.

[11] S.I. Troyanov, A.A. Goryunkov, E.I. Dorozhkin, D.V. Ignateva, N.B. Tamm, S.M. Avdoshenko, I.N. Ioffe, V.Y. Markov, L.N. Sidorov, K. Scheurel, E. Kemnitz, J. Fluorine Chem. 128 (2007) 545–551.

[12] N.S. Ovchinnikova, D.V. Ignateva, N.B. Tamm, S.M. Avdoshenko, A.A. Goryunkov, I.N. Ioffe, V.Y. Markov, S.I. Troyanov, L.N. Sidorov, M.A. Yurovskaya, E. Kemnitz, New J. Chem. 32 (2008) 89–93.

[13] E.I. Dorozhkin, A.A. Goryunkov, I.N. Ioffe, S.M. Avdoshenko, V.Y. Markov, N.B. Tamm, D.V. Ignateva, L.N. Sidorov, S.I. Troyanov, Eur. J. Org. Chem. (2007) 5082–5094.

[14] 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.B. Boltalina, J. Am. Ceram. Soc. 128 (2006) 12268–12280.

[15] P.J. Fagan, P.J. Krusic, C.N. McEwen, J. Lazar, D.H. Parker, N. Herron, E. Wasserman, Science 262 (1993) 404–407.

[16] A.D. Darwish, A.K. Abdul-Sada, A.G. Avent, Y. Lyakhovetsky, E.A. Shilova, R. Taylor, Org. Biomol. Chem. 1 (2003) 3102–3110.

[17] E.I. Dorozhkin, D.V. Ignateva, 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.B. Boltalina, Chem. Eng. J. 12 (2006) 3876–3889.

[18] I.E. Kareev, I.V. Kuvychko, S.F. Lebedkin, S.M. Miller, O.P. Anderson, S.H. Strauss, O.V. Boltalina, Chem. Commun. (2006) 308–310.

[19] N.B. Shustova, I.E. Kareev, I.V. Kuvychko, J.B. Whitaker, S.F. Lebedkin, A.A. Popov, L. Dunsch, Y.-S. Chen, K. Seppelt, S.H. Strauss, O.V. Boltalina, J. Fluorine Chem. 131 (2010) 1198–1212.

[20] N.B. Shustova, I.V. Kuvychko, D.V. Peryshkov, J.B. Whitaker, B.W. Larson, Y.-S. Chen, L. Dunsch, K. Seppelt, A.A. Popov, S.H. Strauss, O.V. Boltalina, Chem. Commun. 47 (2011) 875–877.

[21] O.V. Boltalina, A.Y. Lukonin, J.M. Street, R. Taylor, Chem. Commun. (2000) 1601–1602.

[22] I.V. Kuvychko, A.A. Streletskii, N.B. Shustova, K. Seppelt, T. Drewello, A.A. Popov, S.H. Strauss, O.V. Boltalina, J. Am. Ceram. Soc. 132 (2010) 6443–6462.

[23] N.B. Shustova, D.V. Peryshkov, I.V. Kuvychko, Y.-S. Chen, M.A. Mackey, C.E. Coumbe, D.T. Heaps, B.S. Confait, T. Heine, J.P. Paige, S. Stevenson, L. Dunsch, A.A. Popov, S.H. Strauss, O.B. Boltalina, J. Am. Chem. Soc 133 (2011) 2672–2690.