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ScienceDirect
Mendeleev Commun., 2006, **16(3)**, 159–161

Mendeleev
Communications

C_{60} fluorination with rare earth metal tetrafluorides: an extreme PrF_4 case

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DOI: 10.1070/MC2006v016n03ABEH002332

The fluorinating ability of LnF_4 towards fullerene C_{60} is shown to gradually increase in the series $CeF_4 < TbF_4 < PrF_4$; the latter compound, used for fluorination of fullerenes for the first time, exhibits remarkably strong fluorinating properties yielding hyperfluorinated species $C_{60}F_{n>60}$, with n up to 100.

For several decades metal fluorides were routinely used in fluoroorganic synthetic chemistry, resulting in many cases in the higher selectivity than elemental fluorine.[1,2] More recently, reactions of fullerenes with metal fluorides were also shown to exhibit high selectivity with respect to the formation of a single isomer ($C_{60}F_{18}$,[3] $C_{74}F_{38}$[4]) or very limited number of isomers for a specific composition ($C_{60}F_{36}$[5]). We demonstrated that a judicious choice of the high-valence metal fluorides based on their relative stabilities and oxidising fluorinating ability may result in the control over the fluorination degree in a fullerene.[6] This methodology allowed us to make significant progress in developing the synthesis of fluorofullerenes with low F content.[7–10]

In this work, the first study of the reaction between PrF_4 and C_{60} is reported. In addition, the earlier reported reactions of fullerene with CeF_4[11–13] and TbF_4[14] were also carried out here. We took advantage of the availability of all three reagents prepared using an efficient room-temperature synthetic method.[15] This method was shown to be superior as compared to the earlier reported procedures since it allows one to avoid undesirable formation of the mixed valence fluorides $Ln^{III,IV}F_{4-x}$, which is well documented in the literature.[16–18] Therefore, we were able to perform a direct comparative study of the fluorinating ability of these three reagents, which represent the only known tetrafluorides of rare earth metals.

The compositions of the synthesized LnF_4, which represent solid colourless compounds, were determined by chemical analysis, supported by mass balance data and characterized by X-ray powder diffraction analysis. In a typical synthesis, a finely ground mixture of [60]fullerene (C_{60}, 99.98%, Term USA) and a 45–54-fold molar excess of the corresponding LnF_4 was prepared in a dry box, loaded in the nickel boat, which was placed in a glass tube and heated in a dynamic vacuum (0.1 Pa) for several hours (the details of the experiments are presented in Table 1).

Table 1 Experimental conditions for reactions of C_{60} with LnF_4, where Ln = Ce, Tb or Pr.

LnF_4	$m(C_{60})$/mg	$n(LnF_4)/n(C_{60})$	T/°C	t/h	Yields of products		Observed main products[a]
					m/mg	C_{60} (wt.%)	
CeF_4	20.0	50	310	2	no reaction	—	—
			350	22	4.6	17	$C_{60}F_{36}$
TbF_4	12.5	54	310	5	2.9	27	$C_{60}F_{42-44}$
PrF_4	10.7	45	220–270	3	2.2	21	$C_{60}F_{42-100}$
	15.3	54	290	12	explosion	—	

[a] Determined by mass spectrometry.

The sublimed products were collected from the reactor walls as yellow (in CeF_4 reaction) or off-white powders (in TbF_4 and PrF_4 reactions) by scraping. Molecular compositions were determined by electron ionization (EI, 20–70 eV, Fisons Ins.)

and electrospray ionization (ESI, negative ions, $CHCl_3$ was used as a solvent, LCQ–DUO, TermoElectron) mass spectrometry. White reaction residues were lanthanide trifluorides (CeF_3, TbF_3 and PrF_3), according to the X-ray powder diffraction analysis, and occasionally unreacted C_{60} was also present. Mass spectrometry and HPLC analyses of the residues did not reveal the presence of trace amounts of fluorofullerene products.

The overheating of a reaction mixture containing TbF_4 led to a rapid and vigorous reaction, which resulted in the ejection of the reacted and unreacted powders from the reaction zone.[14] Therefore, in all our experiments, the temperature of the reaction mixture was raised very slowly and only up to the optimal value, at which sublimation of the considerable amounts of products in the cold reactor zone was noted. This fact, as well as the use of very small batches of fullerene per synthesis (10–20 mg), account for quite low yields (*ca.* 20%, Table 1). This does not indicate, however, that these reactions cannot give sufficiently high yields under different conditions. For example, in our previous work with CeF_4,[13] the optimised conditions (450 °C, 3 h) for the synthesis of $C_{60}F_{36}$ afforded 65–70% yields. In this study, our primary goal was to learn what products can form at the lowest reaction temperatures.

In the case of the CeF_4 reaction, the yellow products began subliming at 350 °C. The dominating component of the fluorinated products was $C_{60}F_{36}$, as shown by NI-ESI mass spectrometry. This result is in a good agreement with our earlier data,[11–13] *i.e.,* in the wide temperature range (350–450 °C), a highly selective synthesis of $C_{60}F_{36}$ occurs.

TbF_4 started to react with C_{60} at 310 °C producing the off-white solid in the cold end of the reactor. The product consisted of highly fluorinated fullerenes $C_{60}F_{36–44}$. The predominant formation of $C_{60}F_{44}$ [NI-ESI mass spectrum in Figure 1(*a*)], as in the reported by us reaction with AgF_2,[6] indicates that these two metal fluorides have very similar fluorinating strength and potentially both reactions can be developed into highly selective synthesis of $C_{60}F_{44}$. In our earlier work with TbF_4,[14] a wider distribution of the products was probably due to the higher reaction temperature or presence of $Tb^{III,IV}F_x$ which may decrease fluorinating ability of TbF_4 and shift the product distribution towards lower n(F) in $C_{60}F_n$.

Of the three studied lanthanoid tetrafluorides, PrF_4 was expected to be the most reactive compound.[6] It is known that PrF_4 is less thermally stable than TbF_4; its decomposition (in the N_2 atmosphere) occurs at 90 °C, which is 100 degrees lower than TbF_4.[19] Therefore, it is not surprising that, in our first experiment with PrF_4, the C_{60} fluorination began at much lower temperature (220 °C) than with the other two reagents and proceeded smoothly upon further heating to 270 °C. In the second experiment, heating of the reaction mixture to 290 °C, *i.e.*, higher by only 20 °C than in the first experiment, led to the sudden ejection of the solid from the boat and its spreading on the reactor walls. Apparently, the previously observed explosion-like reaction of C_{60} with TbF_4 at 350 °C,[14] and similar behaviour of PrF_4, but at lower temperature, 290 °C, have similar nature. We earlier speculated that, in case of TbF_4, it was caused by the rapid evolution of highly active atomic fluorine. This conclusion is consistent with the results of the more recent study of the TbF_4 thermolysis,[20] in which atomic fluorine was identified mass-spectrometrically as the main gas-phase component released in the 330–430 °C range. It is feasible that mechanism of decomposition of PrF_4 does not differ significantly from that of TbF_4, and its thermolysis also occurs *via* evolution of atomic fluorine. Hence, PrF_4 can be tentatively regarded as a potent thermal source of atomic fluorine, and its use in the synthesis can be advantageous as compared to TbF_4 due to the lower decomposition temperature. Extensive literature on the use of atomic fluorine as a reactive chemical species is mainly based on the electrochemical,[21] electrical, microwave or radiofrequency discharge, plasma, photochemical or thermal methods of generation of atomic fluorine,[22] which are all technically very demanding to be routinely applied in a non-specialised research lab, while handling of the solid powder of PrF_4 will only require basic inert atmosphere conditions and moderate heating.

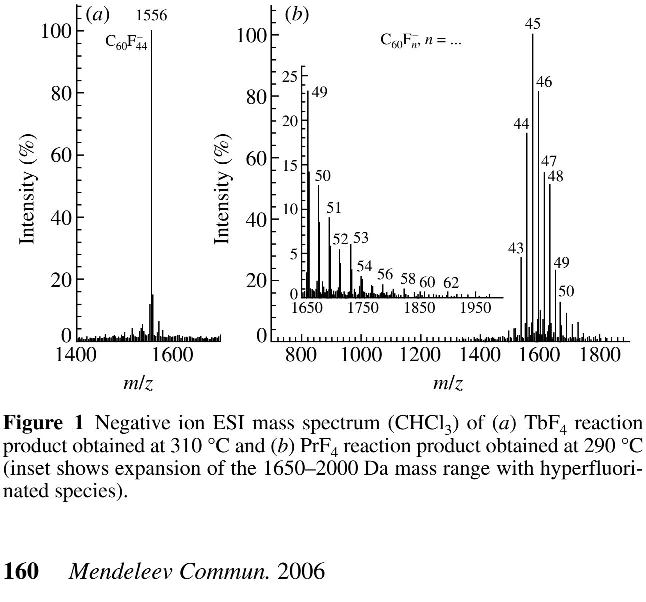

Figure 1 Negative ion ESI mass spectrum ($CHCl_3$) of (*a*) TbF_4 reaction product obtained at 310 °C and (*b*) PrF_4 reaction product obtained at 290 °C (inset shows expansion of the 1650–2000 Da mass range with hyperfluorinated species).

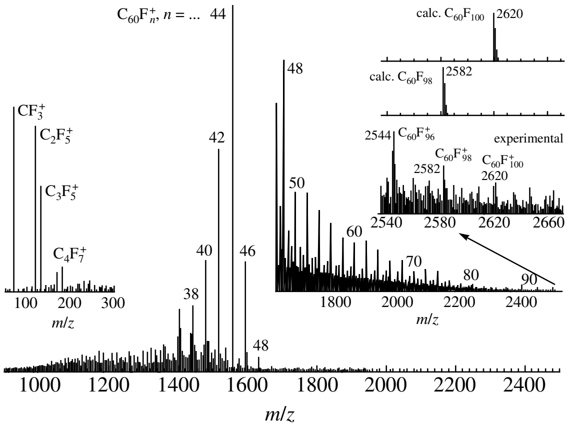

Figure 2 Positive-ion EI mass spectrum of the PrF_4 reaction product obtained at 290 °C. Insets (right) show magnified regions of 1630–2400 and 2540–2660 Da with the identified hyperfluorinated species $C_{60}F_{62–100}$. Inset (top right) shows calculated isotopic distributions for $C_{60}F_{98}$ and $C_{60}F_{100}$. Inset (left) shows low-mass range mass spectrum (60–300 Da) with the identified C_xF_y fragments.

Further confirmation of the similarities between high-temperature reactions of C_{60} with TbF_4 and PrF_4 was obtained from the comparison of the mass-spectrometric data. Results of the NI-ESI mass-spectrometric analysis of the PrF_4-reaction product revealed that both the 270 °C and 290 °C-products contained the species $C_{60}F_{42–64}$, with $C_{60}F_{44–46}$ being predominant components [Figure 1(*b*)]. Positive ion EI MS analysis allowed us to identify the ions $C_{60}F_n^+$ with $36 < n < 100$ (Figure 2).

Molecular species $C_{60}F_{n>60}$ are referred to as hyperfluorides since after addition of 60 fluorine atoms to all 30 double bonds in C_{60} and formation of perfluoro[60]fullerene, $C_{60}F_{60}$, the subsequent F additions will require the carbon C–C bonds to break.[23]

Early literature on fluorofullerenes provides several examples of the reactions in which hyperfluorides of C_{60} were observed. The first such study was reported in 1993, in which elemental fluorine in combination with UV irradiation caused C_{60} to form a series of $C_{60}F_n$, with n up to 102.[23] Use of such powerful fluorinating agent as KrF_2 in anhydrous HF also resulted in hyperfluorination, with the highest observed fluorination degree $n(F/C_{60}) = 78$.[24] Tuinman *et al.*[23] pointed out that use of UV irradiation during F_2 fluorination led to the relative increase in the perfluorinated fullerene contents as compared to the F_2 reaction without UV irradiation: the $C_{60}F_{60}^+$ intensity relative to the most intense ion in the EI mass spectrum reached 1.3%, while in the latter case it was only 0.002%. Similar estimates for our PrF_4 products give even higher value of $I(C_{60}F_{60}^+)/I(C_{60}F_{44}^+) = 3.5\%$ from the EI-MS data, and a more conservative estimate of 2% from the ESI-MS data. These results indicate that PrF_4 can be tentatively considered as one of the strongest fluorinating agents among the known binary metal fluorides, in which atomic fluorine is likely to act as a reactive intermediate in the fluorination process. In support of this hypothesis, we point out that fluorination beyond $C_{60}F_{48}$ is more demanding energetically and sterically, since it must involve subsequent attacks by fluorine of the six remaining double bonds, which were shown to be protected by the surrounding F atoms attached to cage-C atoms to such an extent that the actual open space above such double bond (*ca.* 1.5 Å)[25] is even smaller than the van der Waals diameter of F (2.7 Å).

Relevant cases of the facilitation of the sterically demanding fluorination reactions with the use of atomic fluorine can be found in the literature. An example is formation of the Sherer persistent perfluorocarbon radical from the corresponding precursor with the highly branched structure, which hinders access of any reactive species except for atomic fluorine to the only double bond. The authors even proposed to use this reaction as an indicator of whether atomic fluorine is generated by different fluorinating agents.[26] For example, CF_3OF and XeF_2 were shown to produce atomic fluorine forming the persistent Sherer radical, whereas CoF_3, ClF, ClF_3 or elemental fluorine (F_2) did not at the same temperature.

Previous studies of the C_{60} reactions with elemental fluorine showed the process of fluorine addition to stop abruptly after selective formation of $C_{60}F_{48}$.[27] Attempt to further fluorinate $C_{60}F_{48}$ resulted in the chemical fragmentation to $C_{x<60}F_y$, but not further fluorination of intact C_{60} cage.[28] The fact that in reaction with PrF_4 species $C_{60}F_{n>48}$ are formed readily and relatively abundantly at relatively low temperatures apparently indicate involvement of the more active species than F_2, *i.e.*, atomic fluorine.

In summary, we successfully applied fullerene C_{60} as a chemical probe to determine relative fluorinating strength of the three known binary rare earth metal tetrafluorides LnF_4 (Ln = Ce, Tb or Pr). PrF_4, which was used as fluorinating agent for the first time, demonstrated remarkable fluorinating activity yielding significant amounts of per- and hyperfluorinated fullerenes, which are formed due to interaction of fullerene with the highly reactive intermediate, atomic fluorine, a likely product of PrF_4 thermolysis.

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Received: 15th February 2006; Com. 06/2674