Reaction of silver(I) and (II) fluorides with C_{60}: thermodynamic control over fluorination level

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Dedicated to Prof. Karl O. Christe on the occasion of his 65th birthday

Abstract

Silver(I) fluoride is shown to be a weak fluorinating agent (FA) for C_{60} and gives mainly $C_{60}F_{18}$. Fluorination with silver(II) fluoride yields $C_{60}F_{44}$, a new compound, as the predominant product (>80% in the crude). Fluorination degree of fullerenes in reaction with binary metal fluorides is found to be mainly thermodynamically controlled. The correlation between the level of C_{60} fluorination and oxidising fluorinating strength of the metal fluorides used for fluorofullerene preparations is discussed, permitting development of a self-consistent quantitative scale for inorganic FAs. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mass spectrometry; Fluorination; Fullerene; Fluorofullerene; Silver fluorides; Oxidising fluorinating strength; Thermodynamic control

1. Introduction

Studies on the fluorination of fullerenes have been carried out for the past 10 years [1]. In the early studies, the researchers applied molecular fluorine (F_2) [2–6], fluorides of halogens [7] and fluorides of noble gases [8] which produced mixtures of fluorofullerenes having a broad distribution in the fluorine content. The first single fluorofullerene ($C_{60}F_{48}$) comprising >50% of the product was reported in 1994 by Gakh et al. using an F_2/NaF fluorinating regime [9]. Further progress in this direction was made in 1996, when fluorofullerenes $C_{60}F_{48}$ [10] and $C_{60}F_{36}$ [11] were selectively synthesised in the reactions of C_{60} with F_2 alone and MnF_3, respectively. The latter work has become the starting point of our extensive studies on fluorination of fullerenes with different inorganic agents. So far, experiments have been carried out with a number of binary metal fluorides (MnF_3, CoF_3, CeF_4), some complex salts (K_2PtF_6, K_3CoF_6,) and MnF_3–KF mixture [12]. As a result, the additional fluorofullerenes $C_{60}F_2$ [13], $C_{60}F_{16}$ [14] $C_{60}F_{18}$ [15] and $C_{60}F_{20}$ [12] were prepared and isolated by high pressure liquid chromatography (HPLC), and their structures determined by ^{19}F NMR.

At present, only three fluorofullerenes: $C_{60}F_{18}$, $C_{60}F_{36}$ and $C_{60}F_{48}$ can be prepared in appreciable yields in a one-pot reaction. We now report reactions between C_{60} and silver(I) and (II) fluorides that were studied with the intention of finding synthetic routes for new specific fluorofullerenes. It was anticipated that the reactivity of silver fluorides towards C_{60} would help understanding of how the oxidation state of metal affects the extent to which fluorination of fullerene can proceed.

2. Results

2.1. AgF

According to the electron ionisation (EI) mass spectra (Fig. 1) registered during the in situ fluorination of AgF (molar ratio of AgF:C_{60} was 175:1) at 360 °C, the only product in the gas phase was $C_{60}F_{18}$, along with the unreacted C_{60}, the content of $C_{60}F_{18}$ decreasing rapidly with time.

The product synthesised in the vacuum set up (420–480 °C, the same AgF:C_{60} molar ratio) was separated by means of HPLC to give five fractions with retention times of

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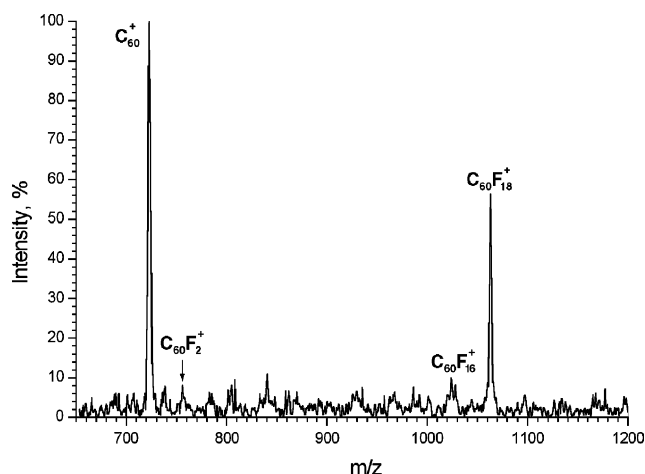*E-mail address*: ovb@thermo.chem.msu.ru (O.V. Boltalina).

Fig. 1. EI mass spectrum registered during in situ fluorination of C_{60} with AgF, reaction time: 1.75 h; temperature: 360 °C; ionisation energy: 70 eV; mass range: 650–1200 amu.

Fig. 3. EI mass spectrum of the AgF_2 product synthesised in a vacuum set up.

7.2, 8.3, 17.3, 37.0 and 61.0 min. These were characterised by EI mass spectrometry as $C_{60}(CF_3)_2$ C_{60} (Fig. 2a), $C_{60}F_4O$ (Fig. 2b), $C_{60}F_{18}$ and $C_{60}F_{18}O$, respectively.

2.2. AgF_2

A number of experiments were carried out in the vacuum set up ($T = 360$ °C) using various AgF_2:C_{60} molar ratios, with the considerable excess of AgF_2 (100-fold quantitative excess). The mass spectral data and HPLC analysis showed that all thus synthesised products mainly consisted of $C_{60}F_{2m}$ with $m = 18$–22 without considerable domination of any species, the reagent ratio having no effect on their
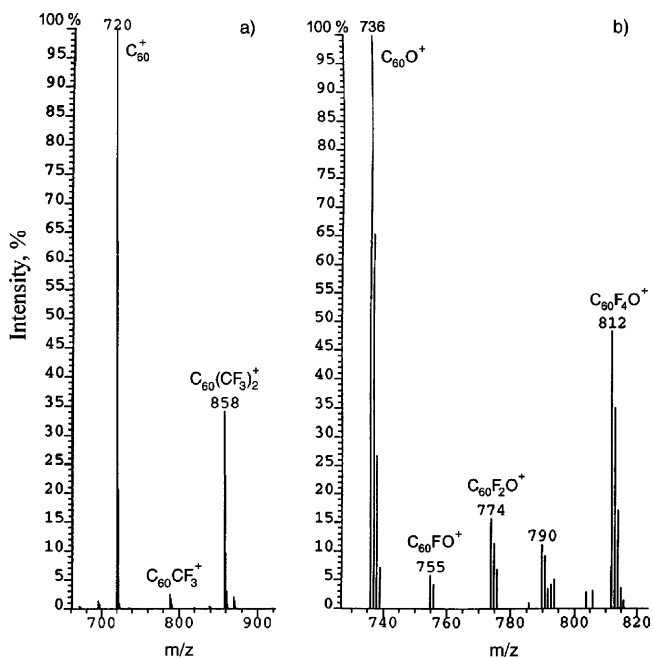

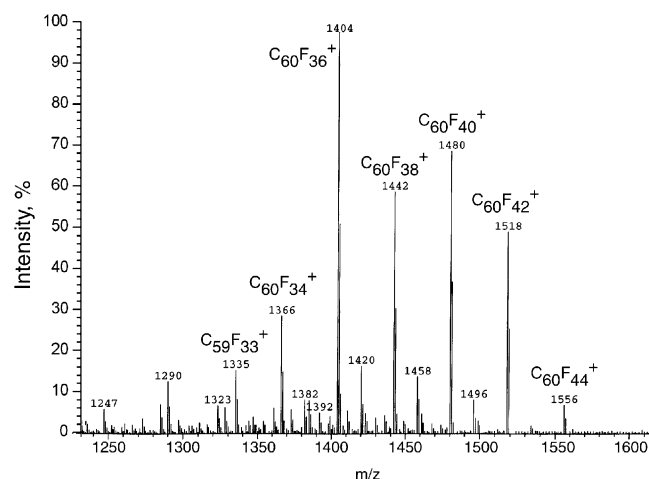Fig. 2. EI mass spectra of the HPLC fractions of AgF product eluting at (a) 7.2 min and (b) 17.3 min.

distribution. A typical mass spectrum is shown in Fig. 3. A broad band in the C–F stretching region (1174 cm^{-1}) in the IR spectrum of the product (not shown) also indicated that a complex mixture of fluorides was formed.

Further reactions with AgF_2 were performed in situ in the mass spectrometer. Initial experiments were carried out in the wide temperature range from 300 to 400 °C in order to study the dynamics of the product distribution in the course of the reaction, which was not possible in the "blind" synthesis in the vacuum set up. Indeed, at 300 °C, we observed the formation of only one fluorofullerene species, $C_{60}F_{44}$, with remarkable selectivity with respect to the satellite fluorides $C_{60}F_{42}$ and $C_{60}F_{46}$ (the major product constituted over 80% of the total ion intensity), this product composition being constant in time for more than 4 h of recording the mass spectra. The fragmentation as seen in the inset to Fig. 4 is very moderate and occurs mainly due
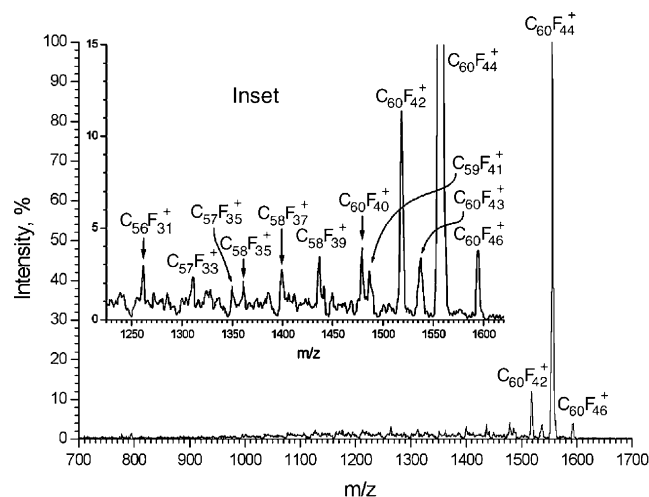

Fig. 4. EI mass spectrum registered during in situ fluorination of C_{60} with AgF_2, reaction time: 2 h; temperature: 300 °C; inset shows an expanded mass spectrum in the mass range of 1250–1600 amu.
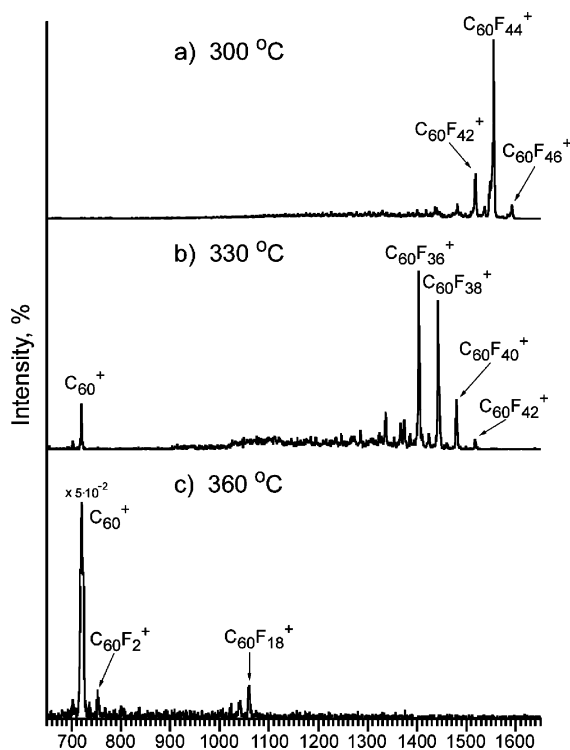
Fig. 5. EI mass spectra registered during in situ fluorination of C_{60} with AgF_2 at 300, 330 and 360 °C, ionisation energy: 70 eV; mass range: 650–1650 amu.

to loss of CF_3 and C_nF_m radicals; it is very similar to that reported earlier by us for $C_{60}F_{48}$ [16].

On raising the temperature to 330 °C, the fluorination level decreased: $C_{60}F_{44}^+$ disappeared from the spectrum, and the most abundant peaks were $C_{60}F_{36}^+$ and $C_{60}F_{38}^+$ (Fig. 5). Further increase in temperature (360 °C) gave rise to even lower fluorinated species such as $C_{60}F_{18}$ and $C_{60}F_2$, but these had much lower intensities. The second experiment was performed at constant temperature (300 °C), i.e. under isothermal conditions, with the purpose of the selective synthesis of $C_{60}F_{44}$. As a result, 7 mg of the product was collected from the collecting plate located in front of the effusion cell of the mass spectrometer. The sample dissolved readily in benzene giving a bright yellow solution from which transparent yellow plates crystallised upon evaporating the solvent. The ^{19}F NMR spectrum (not shown) was complex with many lines, but less than 44 indicating that $C_{60}F_{44}$ has a higher symmetry than C_1.

3. Discussion

The above studies of reaction between C_{60} with silver(I) and (II) fluorides indicate that use of AgF_2 leads to derivatives with much higher fluorine content than does the use of AgF, as one might expect. Silver(I) fluoride was found to be a weak reagent, and apparently of little use for the fluorination of fullerene due to low yields.

As shown by HPLC analysis, in addition to C_{60} and $C_{60}F_{18}$, perfluoroalkyl derivatives of C_{60} constituted some of the fractions of the AgF product. The presence of the CF_3-containing products is normally observed in the fluorofullerene samples prepared at elevated temperatures, which is explained by the formation of CF_3 radicals due to the rupture of fluorinated fullerene skeleton. Therefore, in spite of these disadvantages, the product of the C_{60} fluorination with AgF can be a useful source of perfluoroalkylfullerenes for spectroscopic characterisation. For example, we are currently carrying out structural characterisation of $C_{60}(CF_3)_2$, which will be reported in due course.

Silver(II) fluoride appears to be a much better candidate for the selective production of specific fluorofullerenes. Revealing much stronger fluorinating ability than any metal fluoride examined previously, its reaction with C_{60} afforded selective synthesis of $C_{60}F_{44}$.

Finally, we address the observed remarkable variation in the degree of fullerene fluorination when using various transition or rare-earth metal fluorides or fluorides of the same metal but in different oxidation state, as in case of silver(I) and silver(II) fluorides.

We previously reported [17] on the correlation between the thermodynamic characteristics of metal fluorides and their fluorinating power with respect to [60] fullerene. The relative fluorinating strength of metal fluorides was deduced from the comparison of the equilibrium constants of reaction (1), which can be calculated through the thermodynamic functions of metal fluorides.

$$MF_{n(cr)} = MF_{(n-1)(cr)} + \tfrac{1}{2}F_{2(g)}, \tag{1}$$
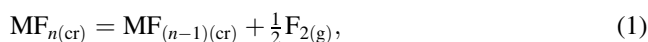
Here, we develop this approach further in an attempt to build a self-consistent quantitative scale of the fluorinating power of the inorganic agents.

Table 1 summarises available data on the products of fluorination of [60] fullerene with fluorinating agents (FAs). Unlike direct fluorination, which gives mainly a broad and continuous distribution of the species with fluorine content centred between 36 F and 48 F, compounds having specific compositions from $C_{60}F_2$ to $C_{60}F_{44}$ are obtained in fluorination with metal fluorides, which are thus more versatile reagents.

In our present consideration, estimations of the oxidising fluorinating activity are based on reaction (2), where atomic fluorine, rather than F_2, is released on decomposition of metal fluoride (see reaction (1)).

$$MF_{n(cr)} = MF_{(n-k)(cr)} + kF_{(g)} \tag{2}$$
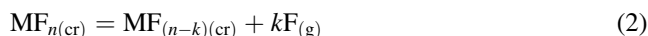
It seems unlikely that upon heating a mixture of metal fluoride and a fullerene, the reaction proceeds via initial formation of molecular fluorine. In the recent studies of the behaviour of unstable metal fluorides (TbF_4) reported by Chilingarov et al. [19], evolution of atomic fluorine was recorded upon heating. Moreover, thermodynamic calculations confirm that the vapour pressure of elemental fluorine

Table 1
Products of the reactions between [60] fullerene and some metal fluorides

FA	Reaction	$\Delta_r H_{298}^\circ(2)$ (kJ/mol)	Temperature of synthesis (°C)	Main products	Reference
F_2	$(1/2)F_2 = F$	79	RT–315	$C_{60}F_{48}$	[9]
TbF_4	$TbF_4 = TbF_3 + F$	168[a]	320	$C_{60}F_{42}$–$C_{60}F_{44}$	[17]
CeF_4	$CeF_4 = CeF_3 + F$	188	330	$C_{60}F_{36}$	[17]
CoF_3	$CoF_3 = CoF_2 + F$	199	350	$C_{60}F_{36}$–$C_{60}F_{40}$	[17]
AgF_2	$AgF_2 = AgF + F$	235	300	$C_{60}F_{44}$	This work
MnF_3	$MnF_3 = MnF_2 + F$	247	320	$C_{60}F_{36}$	[11]
AgF	$AgF = Ag + F$	284	420–480	$C_{60}F_{18}$	This work
CuF_2	$CuF_2 = CuF + F$	333	550–680	$C_{60}F_2$	[18]
FeF_3	$FeF_3 = FeF_2 + F$	356	650–700	$C_{60}F_2$	[18]
CuF	$CuF = Cu + F$	365	–	–	_[b]
VF_3	$VF_3 = VF_2 + F$	384	650	No fluorination	[17]
CrF_3	$CrF_3 = CrF_2 + F$	458	–	–	_[b]

[a] Estimated value.
[b] No data available.

under the fluorination reaction conditions is negligibly small and so can be neglected in a reaction mechanism.

Provided that necessary thermochemical quantities are known [20–23], the most simple way of calculating $\Delta_r H(2)$ is by using Eq. (3).

$$\Delta_r H_{298}^\circ(2) = \Delta_f H_{298}^\circ(MF_{n-k(cr)}) \\ - \Delta_f H_{298}^\circ(MF_{n(cr)}) + k\frac{1}{2}D(F_2) \qquad (3)$$

where $\Delta_f H_{298}^\circ$ is the standard formation enthalpy and $D(F_2)$ is the bond energy in F_2.

This leads to values of $\Delta_r H_{298}^\circ(2)$ spanning the range from 170 to 460 kJ/mol (see Fig. 6 and Table 1). If all the metal fluorides are ordered according to the enthalpy increase for reaction (2), then a correlation with extent of fluorination in the products becomes evident, the most powerful reagent in the series being TbF_4. Comparable high activity was also observed for AgF_2, CoF_3 and CeF_4, all of which give fluorofullerenes in the range of $n(F) = 36$–44; for AgF_2,
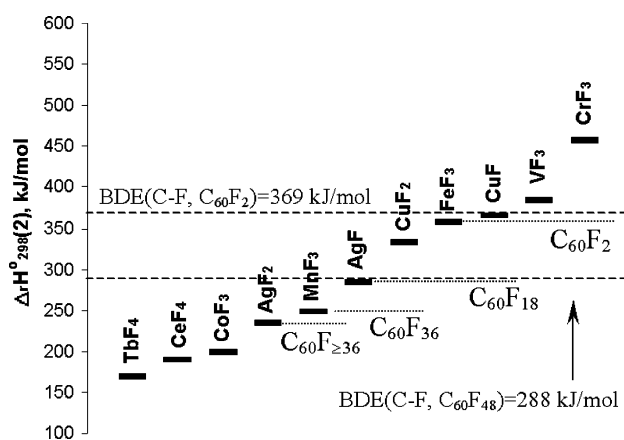
$C_{60}F_{44}$ is a dominant product, whereas CeF_4 yields mainly $C_{60}F_{36}$. Next in the series is MnF_3, which produces mainly $C_{60}F_{36}$ with the small admixture of $C_{60}F_{18}$, whereas AgF is only able to produce $C_{60}F_{18}$. FeF_3 and CuF_2 are known to produce difluorofullerenes at very high temperatures (550–700 °C) in the gas phase [18]. Metal fluorides with $\Delta_r H(2)$ higher than that of CuF_2 and FeF_3 do not fluorinate fullerenes even at elevated temperatures.

Fig. 6 shows also the mean values of C–F bond energy for $C_{60}F_2$ (369 kJ/mol) [18] and $C_{60}F_{48}$ (288 kJ/mol) [24], known from our earlier experiments. Interestingly, fluorination is observed only for reagents for which $\Delta_r H_{298}^\circ(2)$ is lower than BDE (C–F, $C_{60}F_2$). This fits in well with the consideration of fluorination process on the thermodynamic grounds: for the process to be thermodynamically feasible, energy which is required for decomposition of metal fluoride by reaction (2) must be compensated by the energy released due to the formation of the strong C–F bonds. Remarkably, this condition is met in all the fluorination reactions with metal fluorides studied so far (NB: the entropy contribution is neglected in the above consideration).

This permits some tentative predictions for the fluorinating reagents that have not yet been probed experimentally: CrF_3 is expected not to react with fullerenes, whereas CuF may possess some weak activity similar to that of FeF_3.

However, the necessary thermodynamic functions are not well established for all the metal fluorides which were or could be applied to fluorinate fullerenes, thus preventing comprehensive analysis and predictions. For example, information for the rare-earth metal fluorides is very scarce or unreliable; thermodynamic data on complex metal fluorides are practically absent in the literature. In this case, calculation of $\Delta_r H^\circ(2)$, the enthalpy of reaction (2), can be carried out by using Eq. (4) based on the thermochemical cycle (Scheme 1).

The thermochemical cycle involves the potential lattice energy, ionisation potentials and enthalpy of reaction (2) and

Fig. 6. A quantitative scale of the fluorinating power for binary metal fluorides anchored to reactions with C_{60}.

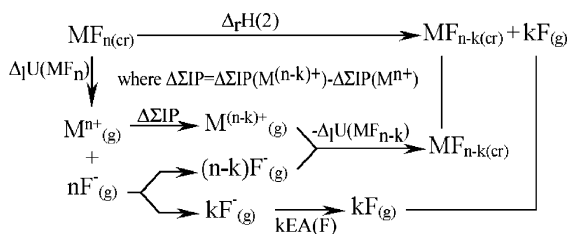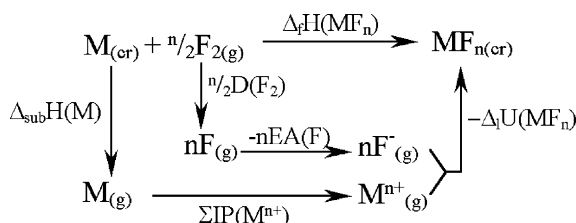Scheme 1. Thermochemical cycle for the calculation of enthalpy of reaction (2).

Scheme 2. The Born–Haber cycle for the calculation of the lattice energy of metal fluorides.

allows one to calculate the latter by using Eq. (4)

$$\Delta_r H^\circ(2) = \Delta_l U(MF_n) - \Delta_l U(MF_{n-k}) + \sum IP(M^{n+}) + kEA(F) \qquad (4)$$

where $\Delta_r H^\circ(2)$ is enthalpy of reaction (2), $\Delta_l U$ the lattice energy, $\sum IP$ the sum of ionisation potentials ($\sum IP(M^{n+}) = IP(M^+) + IP(M^{2+}) + \cdots + IP(M^{n+})$), EA(F) the electron affinity of F, and $D(F_2)$ is the bond energy in F_2.

The lattice energy can be calculated either through the Born–Haber cycle (Scheme 2), which requires data on the formation enthalpies, or by using a theoretical approach [25,26]. It is also possible to estimate the lattice energy from the empirical relations; best known is the Kapustinskii equation [27,28] or recent work by Jenkins and Roobottom [29], giving an empirical equation which allows direct estimations of the lattice energy using data on molecular (formula unit) volume of the ionic salts.

For calculating lattice energies, we used Eq. (5), which is based on the Born–Haber cycle presented in Scheme 2.

$$\Delta_l U(MF_n) = -\Delta_f H^\circ(MF_n) + \Delta_{sub} H^\circ(M) + IP(M^{n+}) + n[\tfrac{1}{2} D(F_2) - EA(F)] \qquad (5)$$
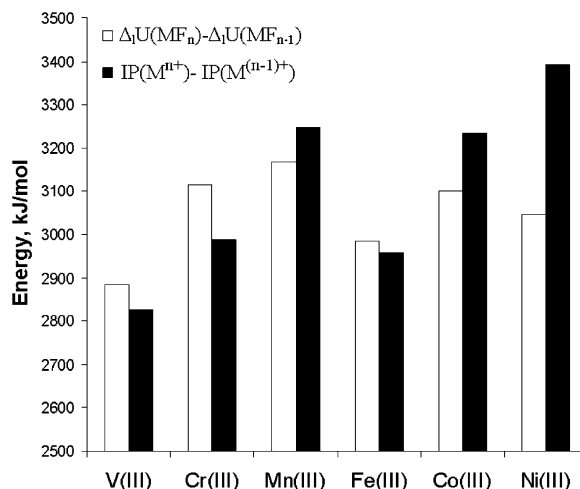

Fig. 7. Histogram showing change in ionisation potentials (IP) and lattice potential energy ($\Delta_l U$) in the first raw transition metal fluorides.

For comparison purposes, estimations with the use of Kapustinskii equation were also made (see Table 2), showing a reasonably good agreement (within 5–8%, or on average 170 kJ/mol) with the values obtained from Eq. (5).

We suppose that in spite of the high absolute uncertainty, such an approach can nevertheless be useful while considering relative fluorinating strength for the unknown binary fluorides or complex metal salts. A systematic error in the absolute values will not affect the trends within the series of similar compounds.

Interesting trends were noted, for example, in the first transition metal series V–Cr–Mn–Fe–Co. Within this group, the lattice energy changes insignificantly due to the small change in the radius of metals, while change in IP is much more dramatic, which is connected with the significant changes in the electronic structure of the metals along the period (Fig. 7). Thus, change in ΔIP mainly determines the change in fluorinating strength, and the strongest FAs among the metal fluorides are characterised by a large value of ΔIP, whereas least active metal fluorides possess small ΔIP. One can apply the observed trend for estimations of the relative activity in the series of rare-earth metal fluorides. For example, if we assume that $\Delta_l U$ for the tetrafluorides of Ce, Tb and Pr change insignificantly, then a comparison of the ΔIP allows one to predict the highest oxidising power for PrF_4.

Table 2
Change in the lattice energy ($\Delta_l U = \Delta_l U(MF_3) - \Delta_l U(MF_2)$) and ionisation potentials ($\Delta IP = IP(M^{3+}) - IP(M^{2+})$) of the first row transition metal fluorides

FA	Reaction	$\Delta_l U$ (kJ/mol)[a]	$\Delta_l U$ (kJ/mol)[b]	Error (%)	ΔIP (kJ/mol)
VF_3	$VF_3 = VF_2 + F$	3120	2884	8.2	2828
CrF_3	$CrF_3 = CrF_2 + F$	3277	3116	5.2	2987
MnF_3	$MnF_3 = MnF_2 + F$	3206	3168	1.2	3248
FeF_3	$FeF_3 = FeF_2 + F$	3183	2985	6.2	2957
CoF_3	$CoF_3 = CoF_2 + F$	3256	3100	5.0	3232

[a] Estimated with the use of generalised Kapustinskii equation [28].
[b] Calculation on the base of thermochemical cycle (Eq. (5)).

4. Experimental

4.1. General experimental procedures

Fluorination reactions were performed in situ in the mass spectrometer as described elsewhere [11], direct analysis of the volatile products in the course of the synthesis thus becoming possible. For the preparations on a larger scale a vacuum set up designed for the high temperature solid-state reactions was used [17]. In both types of experiments, all the manipulations were carried out in a dry box in order to avoid degradation of FAs prior to the reaction with fullerene.

In the experiments on in situ fluorination we applied a magnetic sector mass spectrometer incorporated with Knudsen cell assembly manufactured on the base of the serial MI 1201 (Russia) device with the EI energy being 70 eV. The reagent mixture (fullerene and silver fluoride) was loaded in the nickel effusion cell and heated up to the temperature of the synthesis under vacuum (10^{-4} to 10^{-5} Pa). To characterise the fluorination products, a VG Autospec magnetic double focusing mass spectrometer (UK) using 70 eV EI was employed. HPLC analysis used a 10 mm $\times$ 25 cm Cosmosil Buckyprep column, toluene eluent, flow rate: 4.7 ml/min.

The sample of fullerene C_{60} (purity $> 99.9\%$) was supplied by Term Ltd. (USA). AgF was purchased from Lancaster Synthesis (UK). Sample AgF_2 was prepared by the following procedure. $AgNO_3$ was treated with the elemental fluorine under pressure (11 atm) at 250 °C for 12 h. Then, to remove the volatiles, the product of reaction was pumped at -196 °C and at room temperature and the whole procedure was repeated four times. The product was analysed by X-ray powder diffraction and Raman spectroscopy. The results of the chemical analysis calculated for AgF_2: Ag, 26.0; F, 74.0. Found: Ag, 25.5; F, 71.9.

Acknowledgements

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