NEGATIVE IONS OF FLUOROFULLERENES IN THE GAS PHASE.

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INTRODUCTION

Fullerenes are known to form numerous chemical derivatives due to the presence of many double bonds on the carbon cage. Therefore development of the analytical methods for characterization of the products of chemical reactions of fullerenes has been very important in the fullerene field. Among these methods, mass spectrometry has played a particularly important role. Various MS techniques have also been applied for the determination of the fundamental ionization characteristics of gaseous fullerene molecules and ions.

This work presents the results of our studies of thermal anions of fluorofullerenes by the method of Ion/Molecular Equilibria.

EXPERIMENTAL

Highly fluorinated fullerenes possess much higher volatility than the parent fullerenes, thus the experimental technique that was successfully used for the studies of ion-molecular equilibria involving higher fullerenes and metallofullerenes [1], has been partially modified as follows (Figure 1). A thin Ni tube of 4 mm in diameter and 50-70 mm long is hermetically sealed to the bottom of Pt Knudsen cell. The tube is separated from the cell by a thin foil with small hole. The sample is placed at the bottom of the tube. The temperature of the bottom end is measured by means of Pt/Pt-Rh thermocouple. This construction ensures the temperature difference ΔT of about 100 degrees between the sample and the effusion cell, where thermal negative ions are formed.

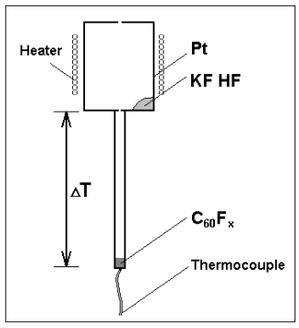

Figure 1.

The thermal ionization (TI) and electron ionization (EI) mass spectra were recorded for the fluoroderivatives of C_{60} of the following chemical composition: $C_{60}F_{18}$, $C_{60}F_{36}$ and $C_{60}F_{44\text{-}48}$.

$C_{60}F_{18}$: No thermal fluorofullerene anions have been observed. Only C_{60}^+ signal was registered in the EI mass spectrum.

$C_{60}F_{36}$: Anions $C_{60}F_{27}^-$-$C_{60}F_{35}^-$ with odd number of fluorine atoms are present in TI mass-spectra, as well as relevant oxygen containing species $C_{60}F_{27}O^-$-$C_{60}F_{35}O^-$. EI mass spectrum shows a dominant molecular ion with only a few fragment ions due to loss of $CF_3\bullet$ and $C_2F_5\bullet$.

$C_{60}F_{44\text{-}48}$: A wide range of negative ions $C_{60}F_{31}^-$-$C_{60}F_{49}^-$, $C_{70}F_{43}^-$ and $C_{70}F_{45}^-$ was recorded utilizing a mixture of fluorofullerenes of the average composition corresponding to $C_{60}F_{46}$ as determined by chemical analysis. Stronger fragmentation compared to the compounds of lower fluorine content may be noted. Monoxides $C_{60}F_xO^-$ together with the peaks corresponding to the relevant fragment ions $C_{59}F_x^-$ were observed.

DISCUSSION

Varying the experimental conditions in our set-up we found that in some cases efficiency of the thermal ion formation depends on the length of the tube used for vaporizing samples.

For fluorofullerenes with high fluorine content thermal anions could be readily obtained regardless the length of the tube. However, fragmentation is considerable, which suggests the decrease in C-F and C-C bond strengths with the number of F atoms in a molecule or an anion.

Much smaller fragmentation was observed in case of $C_{60}F_{36}$ though thermal anions were effectively generated only when a shorter tube (50mm instead of 70mm) was applied. In addition, a prior passivation of the inner surface was found to enable anion formation in this case.

Study of $C_{60}F_{18}$ revealed the degradation of the sample leading to the complete fluorine loss and formation of C_{60} molecules. It is likely that the specific structural features of the $C_{60}F_{18}$ molecule are responsible for this effect, that is location of all 18 fluorine atoms on the one hemisphere of C_{60}.

CONCLUSIONS

We have shown here that it is possible to generate thermal negative ions of highly fluorinated [60]fullerene by ionization on the inner surface of the effusion cell at relatively low temperatures (about 500K). However, considerable fragmentation does not allow one to utilize this method for analytical purposes. On the other hand, it can be used for estimation of the highest degree of fluorination as it was shown earlier for LDI technique [2]. Treatment of the experimental data obtained with $C_{60}F_{46}$ enabled to estimate enthalpies of the reactions of fluorine exchange between the observed anions, which on the average are close to zero. This is probably arises from the close values of C-F bond dissociation energies for these molecules.

REFERENCES

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[2]. Cozzolino R., Belgacem O., Drewello T., Kaseberg L., Herzschuh R., Suslov, Boltalina O., *Eur. Mass Spectrom.*, 1997; **3**; 407.