

THERMAL IONIZATION IN THE FLUOROFULLERENE VAPORS

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In present work a number of samples of fluorofullerenes with different fluorine content were studied by the Ion/Molecular Equilibria method in the context of Knudsen cell mass spectrometry. Highly fluorinated fullerenes are significantly more volatile compared with the parent fullerenes. Thus the experimental technique that was earlier successfully used for studies of refractory inorganic has been partially modified. A thin Ni tube was hermetically sealed to the bottom of Pt Knudsen cell. 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.

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

No thermal fluorofullerene anions were observed for the first sample. Only C_{60}^+ signal was registered in the EI mass spectra. We suppose that specific structural features of the $C_{60}F_{18}$ molecule are responsible for the full fluorine loss and C_{60} molecules formation.

In the EI mass spectra the most intensive peak corresponds to $C_{60}F_{36}$ molecule (100%). Other signals had the following relative intensities: $C_{60}F_{34}$ (40%), $C_{60}F_{38}$ (1%), $C_{60}F_{40}$ (0,5%). Only $C_{60}F_{27}^-$ - $C_{60}F_{35}^-$ anions with odd number of fluorine atoms were observed in the TI mass spectra. It is notable, that the signal $C_{60}F_{33}^-$ was dominant (100%) in comparison with $C_{60}F_{31}^-$ (50%), $C_{60}F_{29}^-$ (10%), $C_{60}F_{35}^-$ (6%), and $C_{60}F_{27}^-$ (5%). If one supposes that these ions are formed through direct electron attachment, then the particles $C_{60}F_{33}$, $C_{60}F_{31}$, and $C_{60}F_{29}$ should have higher electron affinity than $C_{60}F_{35}$.

A wide range of negative ions $C_{60}F_{37}$ - $C_{60}F_{47}$ was recorded utilizing a mixture of fluorofullerenes of the average composition corresponding to $C_{60}F_{46}$ as determined by chemical analysis. In contrast to previous sample a number of additional anions with broken fullerene cage were observed. Obviously these "fragment" ions form due to CF_2 and C_2F_4 loss in the act of ionization process. A correlation can be made with the fact that highly fluorinated species are favorably disposed towards fragmentation under EI. Probably the reason is lower C-C bond dissociation energies compared with less fluorinated molecules.