Solid-phase reactions of C_{60} as a method for generation of gaseous thermal anions of fullerene derivatives

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Ionic components of the vapor above nonvolatile inorganic compounds is being used for a long time for study of the energetics of negative polyatomic ions by means of Knudsen cell mass spectrometry [1]. Chemical equilibrium with respect to various ion/molecule and ion/ion reactions, established inside the effusion cell, gives the way for applying thermodynamics for obtaining the values of electron affinities (EA's) and bond dissociation energies. Later this method, named Ion/Molecule Equilibria – Knudsen Cell Mass Spectrometry (IME-KCMS), was successfully applied for determination of the EA's of higher fullerene molecules C_n in the wide range of carbon index [2].

Attempts to utilize IME-KCMS for fluorine containing fullerene derivatives were long restrained by partial fluorination of the inner surface of the effusion cell, decreasing its work function and thus lowering the efficiency of surface ionization. In the present work we offer the way of solving this problem by utilization of the reaction surface of solid phase reactions between fullerene and solid inorganic fluorinating agents, containing alkali metals ($KMnF_4$, K_2PtF_6, KF-CoF_3, ets) as a surface on which formation of negative ions occurs. Presence of alkali atoms provides low enough work function of the surface during enough long time. Transition metal fluorides MeF_n are known to react with solid fullerene to produce gaseous fluoroderivatives [3]. In present case they serve as a source for molecules (fullerene derivatives) to be ionized, and are conducted *in situ* in the effusion cell at direct contact of reagents as well as through the vapor phase of fullerene (see Fig.1). The latter allows to raise working temperature up to the values, at which utilization of thermal anions of metal fluorides MeF_n^- as standards for obtaining the absolute values of energetic characteristics from the reactions of the type:

$$C_{60}F_n + MeF_4^- = C_{60}F_{n+1}^- + MeF_3.$$

The experiments showed that only anions with odd numbers of fluorine atoms are seen, while neutral species contain exclusively even numbers of F. This fact makes it impossible to study reactions of electron exchange between anions and molecules, and thus direct determination of the EA differences for the fluorofullerenes of different chemical composition. Instead, equilibrium constants for the neutral fluorine exchange reactions were successfully measured:

$$C_{60}F_n^- + C_{60}F_k^- = C_{60}F_{n+1}^- + C_{60}F_{k-1}^-,$$

$$C_{60}F_n^- + 2MeF_k = C_{60}F_{n+1}^- + 2MeF_{k-1}.$$

We also managed to register trifluoromethylated anions in the gas phase of pre-synthesized $C_{60}(CF_3)_m$ compounds, loaded in the effusion cell. Wide range of molecules with different number of CF_3 groups observed in the vapor allowed to study the following electron exchange reactions:

$$C_{60}(CF_3)_m + C_{60}(CF_3)_k^- = C_{60}(CF_3)_m^- + C_{60}(CF_3)_k,$$

and determine relative EA's for $C_{60}(CF_3)_m$ molecules.

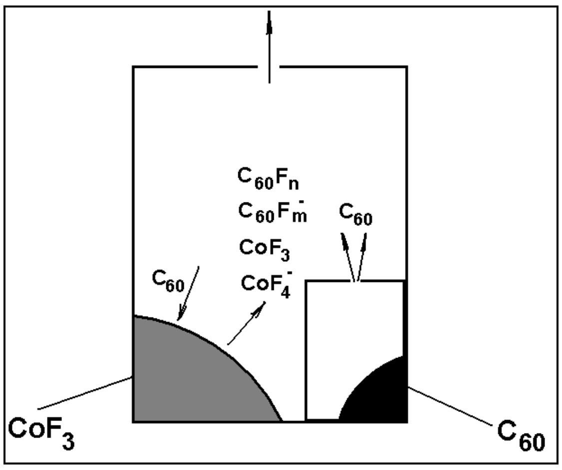

Fig.1

References

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