Journal of Thermal Analysis, Vol. 45 (1995) 1205-1210

THERMAL PROPERTIES OF Fe-FULLERENE SYSTEMS
Is reaction C_{60}+Fe → Fe@C_{60} in solid fullerite possible?

P. Byszewski[1,2], *E. Kowalska*[1] *and R. Diduszko*[1]

[1]Institute of Vacuum Technology, 00–241 Warsaw, ul. Długa 44/50
[2]Institute of Physics PAN, 02–628 Warsaw, al. Lotników 32/46, Poland

Abstract

Iron in the fullerite lattice binds fullerenes in a sandwich type $C_{60}FeC_{60}$ complexes. At the concentration $C_{60}Fe_2$ it crystallizes in the monoclinic lattice. The structure is thermally unstable, with the energy release of 606 kJ·mol^{-1} it returns to fcc lattice. Two possible sites in the reconstructed fcc lattice are discussed, Fe bond to C_{60} and Fe inside the C_{60} cage.

Keywords: fullerene

Introduction

Fullerene is a new allotropic form of carbon. The most symmetric molecule consists of 60 carbon atoms which arranged in a nearly spherical structure of icosaedral symmetry constructed of twelve pentagons and twenty hexagons. All the pentagons are isolated from each other and each of them is surrounded by the hexagons only, the construction of the C_{60} fullerene requires that hexagons touch hexagons and pentagons. It introduces two types of carbon bonds: single ones common for hexagons and pentagons (C–C) of the length $d_{56}=1.45$Å and double ones (C=C) of the length $d_{66}=1.4$Å [1] at a border of two hexagons. This difference of the bonds is reflected in the nonuniform distribution of electrons on the surface of the fullerenes [2]. All the bonds in this model of the molecule are saturated and it can be expected that fullerenes are relatively inactive chemically. In the solid state, C_{60} crystallizes in the cubic close packed lattice with $a=14.14$Å where every molecule is surrounded by twelve nearest neighbours [3]. The influence of the distribution of electrons on the molecules is already seen in the solid, what induces relative orientation of C_{60}–C_{60} molecules below 260 K [4]. The chemical activity of C_{60} has been investigated in experiments selectively utilizing activity of fullerenes. Preparation of superconducting intercalates $C_{60}A_n$ (A=K, Rb and some combination of other metals) [5] relayed on the electronegativity of the molecule and possibility of introducing the metal(s) to the van der Waals gap. Oxidation and functionalization of C_{60} [6, 7] proved that C=C double bonds could be selectively broken and used for binding of different groups. Some of the experiments on hydro-

0368–4466/95/ $ 4.00

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genation of fullerenes were interpreted in terms of delocalized [8] C_{60}–H_n bonds while other as localized [9]. The deficiency of electrons at pentagons sites of C_{60}, suggests that bonds with transition metals of the type in metallocenes could also be expected. The separate class of fullerenes consists of 'endohedral' M@C_{60} these molecules consists of outer carbon shell containing a metal inside [10]. Though several of those molecules had been already 'built', the method used had been rather inefficient, for they had been obtained in the electric arc between carbon electrodes doped with the metal oxides. We present here some of the results of investigation of C_{60}–Fe system. The system seemed to be of much interest because in between of the variety of the position of iron in the C_{60}-based lattice one could be tentatively interpreted as iron occupying the free space inside the fullerenes. In our investigations differential scanning calorimetry (DSC, TG), X-ray diffraction, Moessbauer spectroscopy, infrared absorption and ESR methods were applied, of which the thermal analyses results are discussed here.

Experiment

The transition metals Fe, Co, Ni enter into the coordination compounds – metallocenes – of a general formula $M\mathrm{cp}_2$ where M=Fe, Co, Ni, and $cp=C_5H_5$ cyclopentadien. In these compounds metal is an electron donor and *cp* an acceptor, it could be thought that similar compounds could be formed with fullerenes substituting *cp*. As an iron source ferrocene was used. Both fullerenes and ferrocene are soluble in toluene and crystallites of composition $C_{60}(\mathrm{Fecp}_2)_2$ can be grown from the toluene solution [11]. The ferrocene molecules are built in between C_{60} molecules, otherwise they do not enter chemical reaction with C_{60} at room temperature (in contrast to nickelocene and cobaltocene [5]). This structure is thermally unstable and if annealed in attempt to activate the ligands exchange reaction, ferrocene evaporates. On the DSC run of $C_{60}(\mathrm{Fecp}_2)_2$ (Fig. 1) above 130°C an endothermic effect was registered. The effect was related to the decomposition of the sample and reconstruction of the cubic structure of the fullerite. A mass loss observed by TG measurements confirmed that whole ferrocene sublimed from the fullerite in this transformation. The thermal effects allowed to calculate the fullerene–ferrocene bonding energy which was 164 $\mathrm{kJ\cdot mol^{-1}}$ Fecp_2. This value together with the infrared absorption points to the nature of C_{60}–Fecp_2 bonding, probably by the hydrogen–C_{60} interaction. The temperature required for the ligands exchange reaction is higher than the decomposition temperature of $C_{60}\mathrm{Fecp}_2$. Since the experiments were aimed to decompose ferrocene (which is stable up to 450°C) when it was built into the fullerite structure, we had to find out the experimental conditions enabling the reaction of breaking the Fe–cp bonds of ferrocene dissolved in the fullerite, hoping that the cyclopentadiens might be substituted with C_{60}. If by the thermal diffusion ferrocene could enter fullerite lattice, then higher temperatures could bersed. The results of such experiments are shown in Fig. 1. The DSC run reg-

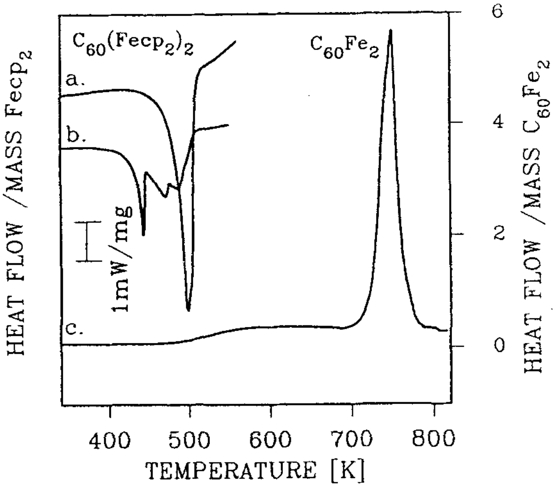

Fig. 1 The DSC runs of: a. decomposition of $C_{60}(Fecp_2)_2$ compound; b. formation of $C_{60}(Fecp_2)_2$ from the mixture of $C_{60}+2Fecp_2$ and its decomposition; c. exothermic transition in $C_{60}Fe_2$

istered during annealing of the mixture of $C_{60}(Fecp_2)_2$ revealed three thermal effects: 1. ferrocene melting, 2. $C_{60}+2Fecp_2 \rightarrow C_{60}(Fecp_2)_2$, 3. decomposition of $C_{60}(Fecp_2)_2$. This experiment proved that C_{60}(ferrocene)$_2$ can be prepared by the thermal diffusion of $Fe(C_5H_5)_2$ to C_{60}. Thus to decompose ferrocene in C_{60} lattice one has to saturate it with the gaseous ferrocene and anneal to the required temperature. The process has to performed in the temperature range 250–400°C (above the decomposition of $C_{60}(Fecp_2)_2$ and below decomposition of pure ferrocene) in sealed ampoules to prevent evaporation of ferrocene (Fig. 2). The solid product of the reaction exhibited a new crystalline structure based on fullerenes and iron. The X-ray diffraction reflexes which were new in the product could be indexed if one assumed that $C_{60}FeC_{60}$ (Fig. 3a) complexes were formed and arranged in the monoclinic lattice with the basal plane shown in Fig. 4, with the following lattice parameters: $a=24.3$Å, $b=12.6$Å, $c=17.1$Å, $\beta=96.9°$. In this structure every C_{60} molecule is surrounded by four Fe ions what corresponds to a formula $C_{60}Fe_2$ of the new compound, with no iron bridging the layers stacked in the ABC... order. The Moessbauer spectroscopy proved that iron is ionized, as in ferrocene at the state of Fe^{2+}, and suggests that it is located opposite to pentagons [12].

This structure is again thermally unstable, above 430°C it undergoes an irreversible exothermic transition with the enthalpy change of $\Delta H=606$ kJ·mol^{-1} $C_{60}Fe_2$ (Fig. 1) when the fullerite cubic lattice is reconstructed. The lattice constant is increased by 0.16Å as compared to pure C_{60} and was found to be $a=14.3$Å. This small change of the unit cell is due to iron presence in the structure. The Moessbauer spectroscopy suggests, iron is in Fe^{3+} state [12], bound to C_{60} as presented in Fig. 3b.

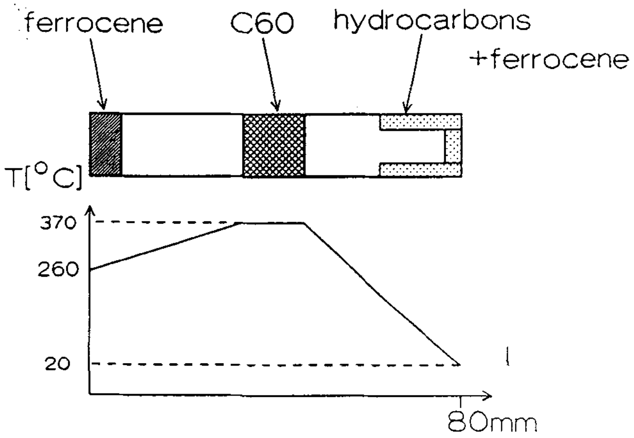

Fig. 2 The ampule and temperatures in the reaction $C_{60}+Fecp_2 \rightarrow C_{60}Fe_2$ +hydrocarbons

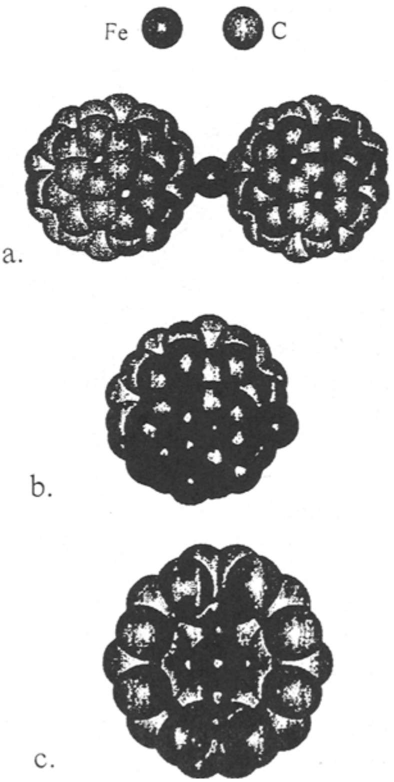

Fig. 3 Three different sites of iron relative to the fullerenes in a. the sandwich type compound with C_{60}–C_{60} distance 10.62 Å; b. the fcc C_{60} based lattice; c. endohedral Fe@C_{60}

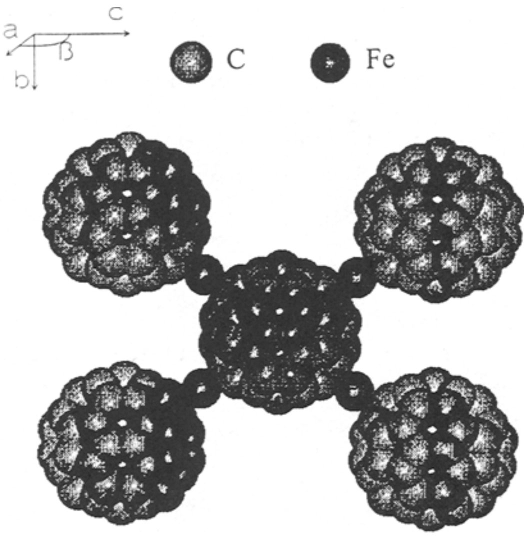

Fig. 4 The arrangement of fullerenes and Fe^{2+} in the monoclinic lattice of $C_{60}Fe_2$

Discussion

In order to form the $C_{60}FeC_{60}$ ferrocene like bonds one can proceed as for the construction of the molecular orbitals of ferrocene [13]. The procedure has to be started with the rearrangement of the π bonds on both fullerenes with the energy expense of at least 5.5 eV which has to be compensated by formation of C_{60}–Fe–C_{60} bonds. For ferrocene this energy is equal to $E=3.15$ eV and because the cyclopentadiens are being substituted by C_{60}, the bonding in the fullerene-iron complex is evidently stronger. Though in the C_{60}–Fe–C_{60} sandwich type compound iron is in a metastable state, for breaking bonds of Fig. 3a is an exothermic reaction of approx. 6 eV/bond. Searching for so highly energetic reaction we have to consider two competing sites of Fe ions in the lattice of Fig. 3b and 3c that is inside of fullerenes. The site until recently we thought as inaccessible in this reaction. Ion inside the fullerene cage is subjected to a high symmetry potential and according to [14], exercises the 'low-frequency rolling', therefore could not be seen in the Moessbauer experiments. In effect the intensity of the Moessbauer doublet, measured for the $C_{60}Fe_2$ sample after annealing it at high temperatures, has drastically decreased [15], though iron concentration estimated qualitatively by X-ray luminescence has not changed during annealing. There is not enough experimental evidence, to prove this suggestion yet it is worthwhile to evaluate such a possibility. The comparison of a radius of Fe^{3+} ion of $r=0.64$Å [16] with carbon hexagonal and pentagonal rings inner diameter of 0.72Å and 0.52Å, respectively, show that the Fe^{+3} ion would rather diffuse through hexagon. The Fe^{3+} ion inside the molecule could increase the effective radius of the ionized fullerene, this in turn could cause the change observed in the lattice constant. This state could be also favourable energetically for all carbon bonds could return to the state of pure C_{60} molecule and the three extra electrons could populate the C_{60}–LUMO derived molecular orbitals. The Fe@C_{60} state could be the most stable one, since endohedrals can be obtained and survive the electric arc process. There is no published information on the depth of such a potential well, it could be above 10 eV as estimated from the described processes.

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This work was partially supported by the State Committee for Scientific Research (KBN) under project No 2P 302 257 03.

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Zusammenfassung — Eisen im Fulleritgitter bindet Fulleren in einem Sandwichkomplex $C_{60}FeC_{60}$. Bei der Konzentration $C_{60}Fe_2$ kristallisiert es in einem monoklinen Gitter. Die Struktur ist thermisch instabil, unter Energiefreisetzung von 606 kJ/mol kehrt es wieder zum fcc-Gitter zurück. Es werden zwei mögliche Orte im wiederhergestellten fcc-Gitter diskutiert, Fe gebunden an C_{60} und Fe innerhalb des C_{60}-Hohlraumes.