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Synthesis of Fullerene Derivatives

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Abstract—This paper presents the results of plasmachemical synthesis of fullerene derivatives with hydrogen, iodine, iridium, platinum, and scandium. The synthesis is carried out under atmospheric pressure in a carbon–helium plasma stream formed by an ac arc in the rf range. © 2002 MAIK “Nauka/Interperiodica”.

The synthesis of fullerene derivatives with H₂, I₂, Sc, Ir, and Pt was carried out in a plasmachemical reactor developed earlier in [1, 2]. The reactor differs considerably from the widely used Kretschmer reactor in that the synthesis occurs under atmospheric pressure in a stream of carbon–helium plasma generated by an ac arc in the rf range. The reactor makes it possible for particles of the introduced substance to stay for a long time in the carbon plasma jet and, hence, become atomized completely. Consequently, this reactor can be used for the synthesis of fullerenes both with light elements and with refractory metals.

In accordance with the concept of the effect of the electron concentration on the formation of fullerenes and fullerene derivatives in a carbon plasma, which was developed in our earlier work [3], we synthesized fullerene derivatives by adding both donors and acceptors of electrons (hydrogen, iodine, scandium, iridium, and platinum). The initial metallic powder or metal wire was placed in a hole ($d = 1.2$ mm) made in one of the electrodes between which the plasma jet of carbon with a metal was formed. Hydrogen and iodine were introduced into the reactor in the form of a gas flow and vapor, respectively, in different temperature regions of the plasma. We tested fullerene-containing soot and fullerenes extracted from it.

An analysis of the x-ray spectra revealed that Ir, Pt, and Sc metals are present in a fullerene-containing soot only in the amorphous state.

The fullerene yield increased upon the introduction of a metal from 4 to 12%. The introduction of iodine virtually nullifies the concentration of fullerenes in the soot.

The electronic absorption spectra for the fullerene extract from soots obtained during the synthesis with the introduction of hydrogen exhibited the following

changes (as compared to the spectrum for a fullerene mixture): a new band appeared at 434 nm and the band at 334 nm was displaced to the UV region by 17 nm. This variation is usually attributed to fullerene complexes with hydrogen of the C₆₀H₂ type [4, 5].

Emission spectroscopy revealed the presence of Sc at a content of the order of 10⁻³% in the fullerene-containing extract.

Highly effective chromatographic separation of the fullerene mixture prepared by extraction from Ir- and Pt-containing soots was carried out in a Cosmosil Buckyprep column. The mass spectra of the separated fractions were measured. It was found that the given extract contains 55% C₆₀, 25% C₇₀, 15% higher fullerenes (mainly, C₇₆, C₇₈, C₈₂, C₈₄, and C₈₆), and 5% oxidized fullerenes C₆₀ and C₇₀.

Mass spectrometry did not reveal the presence of any platinum or iridium derivatives in the extracts separated from Ir- and Pt-containing soots. This can be due to poor volatility of the formed metal compounds. Moreover, Pt- and Ir-containing derivatives involved in soots may be insoluble in organic solvents. In this connection, we made an attempt to convert them into volatile chelate complexes of metals, which are soluble in organic solvents and similar to those described in [6]. Fullerene-containing soots with Pt and Ir (samples I and II, respectively) were treated with acetylacetone (*Hacac*) in solutions of HF (a) and HCl (b) acids during heating, and, then, reaction products (**Ia**, **IIa**, **Ib**, and **IIb**) soluble in organic solvents were extracted from the reaction systems.

The electronic absorption spectra of products **Ia** and **IIa** are shifted to the UV region as compared to samples I and II. The x-ray diffraction pattern of the toluene extract of the Ir-containing product **IIa** contains reflections of fullerene (for small angles) and reflections of

an unknown substance (for large angles); the latter reflections can be associated with Ir complexes.

Toluene extracts of the synthesis products contained fractions of greenish yellow and yellow color which were soluble in protogenic solvents (acetone and alcohol). The electronic absorption spectra of compounds obtained from fullerene-containing soots and the spectra of halogenated iridium acetylacetonates contain bands at 270–280 nm, which are similar to the bands of iridium γ -fluoroacetylacetones but are displaced by 10–15 nm toward the long-wavelength range. The presence of other bands can be associated with the presence of fullerenes in the metal complexes; in addition, the formation of carbon-bonded acetylacetonates and mixed halogenacetylacetonates of metals is also possible.

The results obtained demonstrate that, in the iridium- and platinum-based fullerene-containing soots, iridium and platinum are in the chemically active form. This follows from the fact that the aforementioned reactions with acetylacetone do not occur with the familiar metallic forms of iridium and platinum (compact metal, metallic sponges, and powders). It can be assumed that the active form of Ir and Pt is their oxidized state in the form of insoluble fullerides; however, the results of x-ray diffraction analysis indicate the presence of amorphous particles of a metal in soots, which probably exhibit a high chemical activity.

The experiments described here indicate that the synthesis of metallocomplexes of fullerenes in preparation amounts is a complex problem associated with the donor and acceptor properties of the substances being introduced. Further investigations are required for determination of the relation between the magnitude and the variation of the electron concentration in a plasma upon the introduction of various elements, on

the one hand, and the yield of the resulting fullerene derivatives, on the other. This will be the next step toward the controlled synthesis of fullerene derivatives.

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