ELECTROCHEMICAL PROPERTIES OF METHANO[60]FULLERENE'S CARBONYL DERIVATIVES

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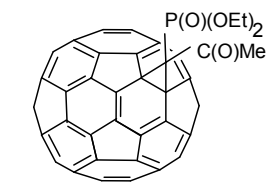
Introduction

Fullerenes are known as redox active chromophores with rather low energy of the lowest unoccupied molecular orbital and are capable to accept up to six electrons per molecule with the formation of stable multianions. Four reversible single-electron reduction stages are registered for methanofullerenes with neutral substituents R и R′ at *exo*-carbon (H, Ph). The π-system of fullerene shell is a reaction centre at the process of an electron transfer. All of the reduction steps are shifted towards negative potentials versus fullerene C_{60}. The stages of electron transfer are characterized by high rate constants and low energy of reorganization (the same order as for pristine fullerene). The electron transfers stages differ in potentials (0.4-0.5 V) therefore the reactions of disproportionation are not typical for anion intermediates and on the contrary reaction of coproportionation are characteristic. A three-membered cycle is stable in temporary scale of voltammetric measurements in anion-radicals, dianions, trianion-radicals and tetraanions of these compounds.

The processes of reduction are changed cardinally at introduction of two ester or two phosphonate or ester and phosphonate substituents in a molecule. The primary anion intermediates are less stable in these cases; the disclosure of three-membered cycle and elimination of addend (reaction of retro-cyclopropanation) occur.

The electrochemical reduction of methanofullerene's carbonyl derivatives **1-7** were studied by cyclic voltammetry and ESR in a combination with *in situ* electrolysis in order to create the generalized conception about a role of the substituents in destabilization and transformations of anion intermediates.



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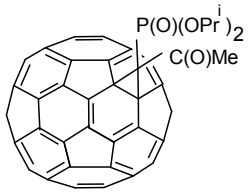

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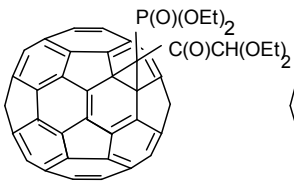

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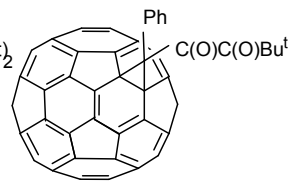

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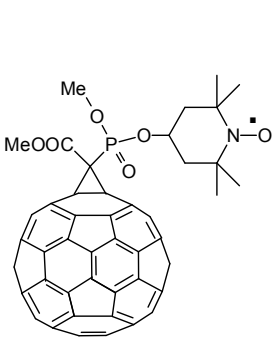

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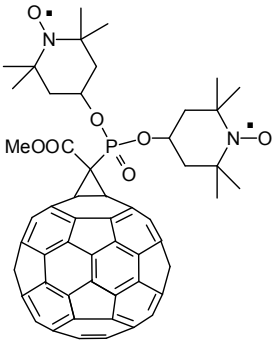

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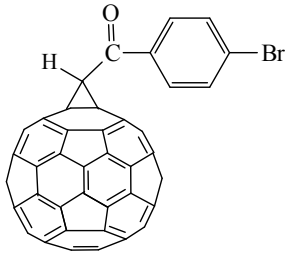

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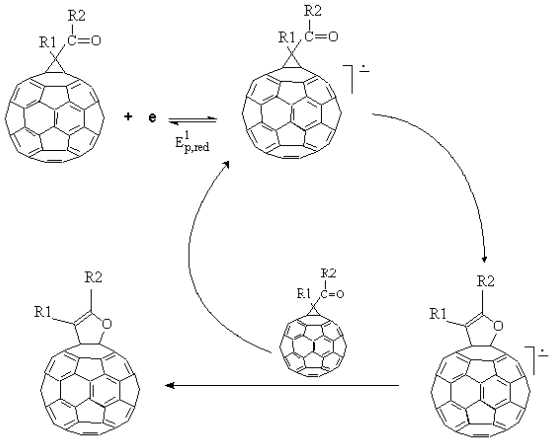
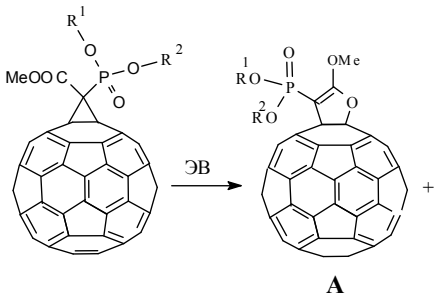
Results and discussion

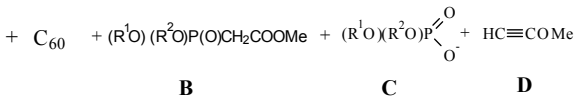
The electrochemical reduction of these compounds on glass-carbon electrode in *o*-dichlorobenzene-DMF (3:1v/v) /0.1M Bu_4NBF_4 medium proceeds in a few stages. At the first stage in all cases the reversible single electron transfer results in formation of radical-anion registered by ESR. The disclosure of cyclopropane fragment occurs with various rates at different reduction stages depending on the nature of the substituent. The nature of final products depends also on the electron-accepting properties of substituents. In compound **7**, which contain keto-group as the substituent, the disclosure is accompanied by elimination of methanogroup with the formation of free fullerenes (reaction of a retro-cyclopropanation).

In contrast the electron transfer in methanofullerenes containing keto- and phosphonate groups **1-4** does not induce the elimination of methanofragment but results in intramolecular rearrangement with the formation of new substituted fullerodihydrofuranes by the chain reaction mechanism (scheme 1).



A four-step reduction of fullerene shell and reduction of nitroxyl group proceed at reduction of mono- and biradical TEMPOL containing dialkoxyphosphoryl(alkoxycarbonyl)methanofullerenes **4**, **5**. The disclosure of three-membered cycle results in two parallel processes: transformation into fullerodihydrofurane and elimination of addends as carbanions, stabilized by protonation and rearrangement into phosphate-ion and substituted acetylene (scheme 2).





The heterogeneous electron transfer on nitroxyl radical at the potentials of third electron transfer on fullerene sphere and homogeneous intramolecular electron transfer from fullerene's dianion is shown using model compounds.

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