

**ELECTROCHEMICAL REDUCTION
OF PHOSPHORYLATED MONO- AND
BIS-METHANOFULLERENES**

V.V.Yanilkin, V.I.Morozov, V.P.Gubskaya,
N.V.Nastapova, L.Sh.Berezhnaya, V.V.Zverev,
I.A.Nuretdinov

A.E.Arbusov Institute of Organic and Physical Chemistry, Kazan Scientific Center of the Russian Academy of Sciences, Arbuzov str.8, 420088 Kazan, Russia. Fax: 7 (8432) 752253. E-mail: yan@iopc.knc.ru

Reactions of electron transfer of new functionally substituted fullerenes derivatives come into notice in connection with the searching of new material and bio-logical active compounds. In a case of methanofullerenes these reactions are important also from the point of view of introduction and taking out of protective groups.

We have studied the processes of electron transfer on the molecule of $C_{60}C[P(O)(OR)_2]_2$ (R = Et (1), i-Pr (2)), $C_{70}C[P(O)(OEt)_2]_2$ (3) and five regio-isomeric bis-adducts of [60]fullerene (*e*, *tr-1*, *tr-2*, *tr-3* and *tr-4* $C_{60}\{C[P(O)(OEt)_2]_2\}_2$, which addends attached to

fullerenes on 6,6-bonds, using methods of cyclic voltammetry, EPR in combination with *in situ* electrolysis in the system o-DCB-DMF (3:1)/0.1M Bu₄NBF₄ (0.1 mol·l⁻¹) and quantum chemistry. Four reduction steps are registered for all compounds in area of more negative potentials for mono-methanofullerenes on 80-110 mV and for bis-methanofullerenes on 120-200 mV and subsequent are fixed at potentials of the relevant peaks C₆₀ and C₇₀.

Table. Reduction potentials (V vs. Fc⁺/Fc) and electron affinity for phosphorylated methanofullerenes. C = 1·10⁻³ mol·l⁻¹, scan rate 100 mV·s⁻¹

Com Pounds	-E _p ¹	-E _p ²	-E _p ³	-E _p ⁴	EA, EV
C ₆₀	0.96	1.40	1.90	2.39	2.65
C ₇₀	0.97	1.39	1.84	2.29	
1	1.04	1.49	1.91	2.40	2.48
2	1.07	1.50	1.90	2.39	
3	1.07	1.49	1.83	2.29	
<i>tr-1</i>	1.12	1.56	1.92	2.41	2.34
<i>tr-2</i>	1.11	1.53	1.92	2.41	2.33
<i>tr-3</i>	1.16	1.60	1.92	2.41	2.27
<i>tr-4</i>	1.16	1.59	1.91	2.41	2.27
<i>e</i>	1.17	1.59	1.92	2.41	2.26

Tr-1 and *tr-2* isomers are reduced under one potential practically, but little (≈ 50 mV) easier than rest isomers. At the first step of the reversible single electron transfer results to formation of anion-radicals, which fixed by the method EPR. At ambient temperature the anion-radicals of *tr-4* regioisomer descends slow elimination one methanofragment to with formation of monomethanofullerene, the anion – radicals of other regioisomers and mono-methanofullerene are considerably more stable.

At transfer of two electrons on a molecule occurs fast elimination of methano addends (retro-Bingel reaction)[1,2]. This process consists in step by step break of two C-C bonds of exo-carbon with fullerenes shell in a combination with step by step transfer of two electrons and proton with formation at the end of the methano-addend carbanion and fullerene dianion. For all investigated compounds the elimination rate is much higher, than for bis(alkoxycarbonyl)- and dialkoxyphosphoryl-(alkoxycarbonyl)methano[60]fullerenes, that allows to offer of diphosphonmethano-group as protective at synthesis of new fullerene derivatives.

Theoretical consideration of electronic structure and electron affinity (EA) by semiempirical method PM3 and methods of density functional theory Perdew-Burke-Ernzerhof (DFT/PBE) with GAMESS and PRIRODA programs was studied. We found on the example of $C_{62}[P(O)(OEt)_2]_4$ and model bismethanofullerenes $C_{62}[P(O)(OMe)_2]_4$ and $C_{62}H_4$ a similar dependency of electron affinity in the gas phase and E_p.

Obviously, the difference of EA and reduction potentials of mono-adducts and regioisomeric bisadducts is not defined by nature of addends but topological particularity of interaction frontal orbitals. This regularity must be observe for all bismethanofullerenes.

This work was financially supported by the Russian Foundation for Basic Research(Project 99-03-32888, 01-03-32181), the Russian Scientific and Technical Program “ Fullerenes and Atomic Clusters”(Project 98008, “Gemo-2”) and by the Academy of Sciences of Tatarstan.

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