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Chain reaction of methano[60]fullerene transformation into dihydrofullerenofurane initiated by single electron transfer

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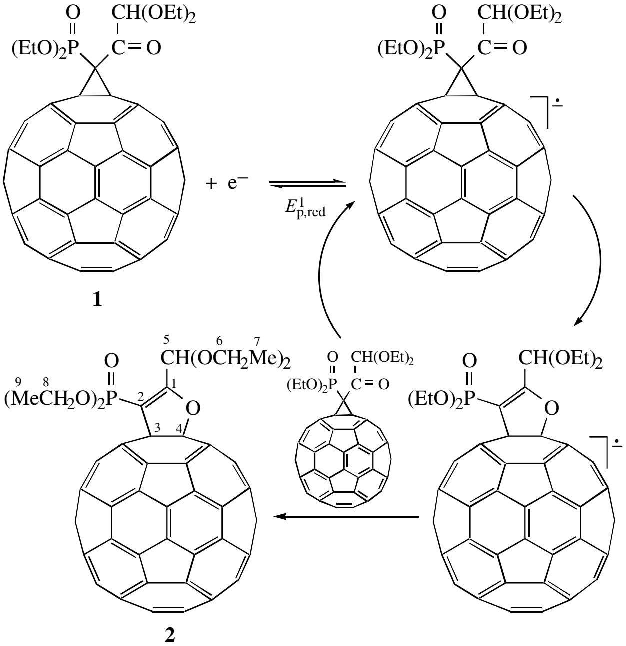
The electrochemical reduction of 61-(2,2-diethoxyacetyl)-61-(diethoxyphosphoryl)methano[60]fullerene accompanied by the opening of a three-membered ring results in the formation of 2-diethoxymethyl-3-diethoxyphosphoryl-3a,61a-dihydrofullereno-[1,2-*b*]furane.

Electron transfer in the electrochemical reduction of methanofullerenes containing substituents capable of negative charge delocalization induce the disclosure of a cyclopropane fragment to result in the elimination of a methano group,[1–4] its migration over the fullerene sphere[2,3] or from one fullerene shell to another.[5] The correlation between these directions is determined by the nature of substituents at *exo*-carbon and experimental conditions. Thus, the reduction of methanofullerenes containing a dialkoxyphosphoryl group and an ester or phosphonate group as the second substituent results in the elimination of a methano group and in the formation of pristine fullerene.[5] The influence of other electron-acceptor substituents at *exo*-carbon on the processes of electron transfer, the stability of anion intermediates and the subsequent transformations is of interest.

Here we report on the electrochemical reduction of 61-(2,2-diethoxyacetyl)-61-(diethoxyphosphoryl)methano[60]fullerene **1** containing a phosphonate group and an electron-acceptor keto group as the second substituent. The study was performed by cyclic voltammetry (CV), ESR in a combination with *in situ* electrolysis and preparative electrolysis.

Six peaks of reduction ($E^{1}_{\mathrm{red}} = -1.03$ V, $E^{2}_{\mathrm{red}} = -1.46$ V, $E^{3}_{\mathrm{red}} = -1.86$ V, $E^{4}_{\mathrm{red}} = -1.97$ V, $E^{5}_{\mathrm{red}} = -2.16$ V, $E^{6}_{\mathrm{red}} = -2.33$ V, *vs*. Fc/Fc$^+$) are observed on CV curves (Figure 1) recorded in *o*-dichlorobenzene–DMF (3:1 v/v)/0.1 M Bu_4NBF_4 on a glass-carbon electrode. The electrolysis at the potential of the first reduction peak immediately in the cavity of the ESR spectrometer results in the formation of radical anions ($g = 1.99997$, $\Delta H = 0.14$ mT), which slowly transform into secondary radical anions ($g = 2.00004$, $\Delta H = 0.08$ mT). The *g*-factors and line widths ΔH of secondary radical anions of compound **1** are more characteristic of fullerene derivatives with five-membered rings, joined to a fullerene sphere at a 6,6-bond. For example, in the case of radical anions of fulleropyrrolidines, $g = 2.0000$, $\Delta H = 0.08$ mT.[6] Based on the data obtained, we supposed the formation of a fullerene derivative with a dihydrofurane group and a chain reaction of methanofullerene **1** (Scheme 1).



Scheme 1

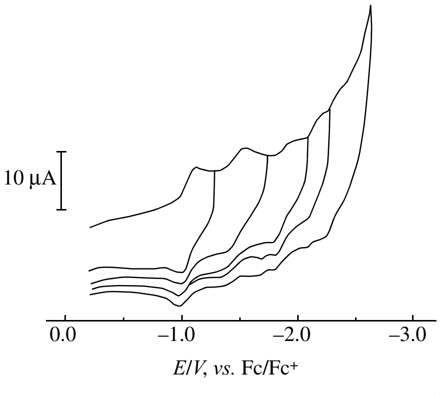


Figure 1 Cyclic voltammograms of methanofullerene **1** (10^{-3} M) in *o*-dichlorobenzene–DMF (3:1 v/v)/0.1 M Bu_4NBF_4 at a glass-carbon electrode. Potential scan rate $v = 100$ mV s^{-1}, $T = 295$ K.

The preparative reduction of methanofullerene **1** was carried out to confirm the product structure and the chain character of its formation. To convert methanofullerene **1** into dihydrofullerenofurane **2** by the chain reaction (Scheme 1), it is necessary to obtain only a small amount of primary radical anions; therefore, we have passed 0.25 F reckoning on methanofullerene **1**. The chromatogram of a sample taken immediately after the electrolysis (Figure 2, sample 1) exhibited a great amount of initial compound **1** and a small amount of a product, which has a longer retention time (Figure 2). After 20 min of 'free-running' mixing the second sample was taken, the chromatogram of which differs from the first one. This time the ratio product/initial compound is practically 1:1 (Figure 2), *i.e.*, the concentration of the initial substance decreases and that of the product increases without electrolysis after the process of generating some amount of primary methanofullerene **1** radical anions. This result testifies the chain character of product formation from the radical anions of compound **1**. Having finished the process of electrolysis, a reaction mixture has been separated from high molecular fullerene products and supporting electrolyte by flash chromatography on silica gel. All spectral characteristics of the pure product completely correspond to the expected compound 2-diethoxymethyl-3-diethoxyphosphoryl-3a,61a-dihydrofullereno[1,2-*b*]furane **2**, and agree with the spectra of other fullero-4,5-dihydrofuranes.[7–10] The yield of the isolated pure product was 37.5%.

The mass spectrum of isolated dihydrofullerenofurane **2** contains peaks with *m*/*z* of 1001 (15), 1001 (40), 1000 (46.7), 973 (35.3), 972 (50.5), 971 (66), 722 (28), 721 (70) and 720 (100). The IR spectrum contains strong absorption bands due to the fullerene shell and the phosphoryl group at 526 and 1251 cm^{-1}, respectively. The band due to the carbonyl group of initial methanofullerene **1** at 1730 cm^{-1} is absent. The UV spectrum of compound **2** contains an absorption maximum at 429 nm, which corresponds to the formation of a monocycloadduct on closed 6,6-bond. The ^{31}P NMR spectrum shows, under conditions of broad band decoupling, one signal with a chemical shift of 11.97 ppm and, without the broad band decoupling, a quintet caused by spin–spin interaction with protons at C^8.

The ^{1}H NMR spectrum contains two triplets from two distinct methyl groups in the region 1.2–1.5 ppm, two multiplets due to methylene protons in the region 4.0–4.3 ppm and a signal due to C^5 at 6.62 ppm. The ^{13}C NMR spectrum contains two *sp*^{3}-carbon atom peaks at δ 73.4 and 103.3 ppm (C^3 and C^4, respectively) and 28 peaks in the *sp*^{2}-carbon atom of fullerene sphere region δ 135.1–148.6 ppm. The carbon chemical shifts of a dihydrofurane ring are observed at 101.7 (C^2) and 167.7 ppm (C^1). The signals of substituent carbons are observed at δ 15.49 (C^7), 16.09 (C^9), 62.29 (C^8), 63.96 (C^6) and 95.69 ppm (C^5). For some carbons the spin–spin interaction with a phosphorus nucleus is shown: C^1 ($^2J_{\mathrm{CCP}}$ 29 Hz), C^2 ($^1J_{\mathrm{CP}}$ 209 Hz), C^3 ($^2J_{\mathrm{CCP}}$ 9 Hz), C^8 ($^1J_{\mathrm{CP}}$ 5 Hz), C^9 ($^2J_{\mathrm{CCP}}$ 7 Hz).

Compound **2** was studied by voltammetry and ESR spectroscopy. Five reduction peaks are detected for this compound ($E^1_{\mathrm{red}} = -1.01$ V, $E^2_{\mathrm{red}} = -1.40$ V, $E^3_{\mathrm{red}} = -1.87$ V, $E^4_{\mathrm{red}} = -2.18$ V, $E^5_{\mathrm{red}} = -2.31$ V). The fifth peak, poorly expressed at a potential scan rate 100 mV s^{-1}, is precisely shown at smaller scan rates (Figure 3). The first and third peaks are ideally reversible and the reversibility of other peaks depends on potential scan rate and reverse potential (Figure 3). The heights of the first four peaks are virtually identical and correspond to a single electron level. It is obvious that there are chemical reactions in the dianion, obtained at the second step of reduction, which do not result in an increase of electron numbers; the potentials of reduction peaks indicate the same. The first electron transfer on the molecule of dihydrofullerenofurane **2** occurs more difficultly than on fullerene C$_{60}$ (40 mV) and it is almost so easy as on methanofullerene **1**. The potential of the second peak virtually coincides with the potential of the second peak of fullerene and lies below the potential of the second peak of methanofullerene **1**. The difference of potentials between the peaks for fullerene derivatives, forming stable anion intermediates, is the same as for fullerene itself. The smaller magnitude of this size for dihydrofullerenofurane **2** is caused by the subsequent fast chemical transformations of the dianion. The subsequent three peaks of reduction of dihydrofullerenofurane **2** are observed at the potentials of third, fifth and sixth peaks of methanofullerene **1**. The peak appropriated to the fourth peak of methanofullerene **1** reductions in this case is absent.

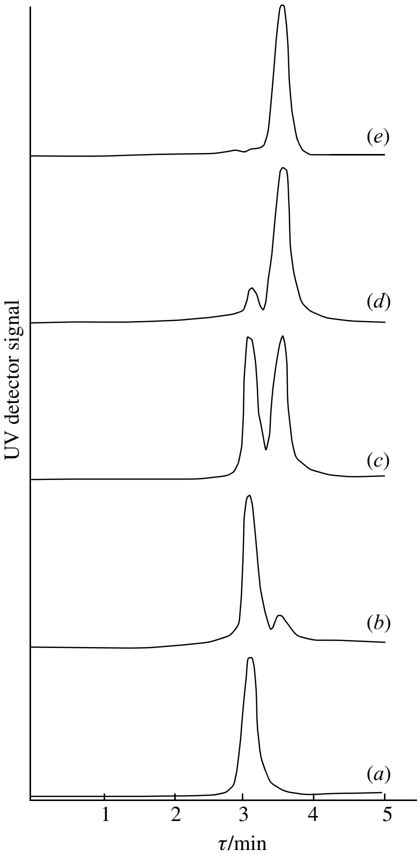


Figure 2 Chromatograms of (*a*) methanofullerene **1** and (*b*)–(*e*) reaction mixture after its electroreduction: (*b*) sample 1, (*c*) sample 2, (*d*) sample 3 (taken after additionally passing 0.15 F) and (*e*) sample 4 (taken after 'free-running' mixing for 20 min).

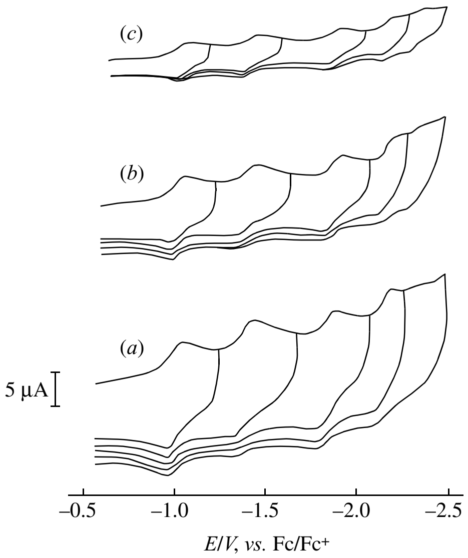


Figure 3 Cyclic voltammograms of dihydrofullerenofurane **2** (10^{-3} M) in *o*-dichlorobenzene–DMF (3:1 v/v)/0.1 M Bu$_4$NBF$_4$ at a glass-carbon electrode at different potential scan rates: (*a*) 100, (*b*) 50 and (*c*) 20 mV s^{-1}. $T = 295$ K.

The reversibility of the first stage and the affinity of reduction potentials of dihydrofullerenofurane **2** and methanofullerene **1** conform to the assumption of a homogeneous reaction of electron transfer from radical anions of dihydrofullerenofurane **2** on a molecule of initial methanofullerene **1** and validity of the above scheme of chain reactions of product formation. The radical anion of dihydrofullerenofurane **2** was generated by electrolysis at the first peak potential immediately in the cavity of the ESR spectrometer; its spectrum coincides with secondary radical anion spectra obtained upon the long reduction of methanofullerene **1**.

Thus, in the reduction of the test methanofullerene, in contrast to phosphorylated methanofullerenes,[4] the ring disclosure is not accompanied by the elimination of a methano group but results in the formation of dihydrofullerenofurane by a chain reaction. The presence of a keto group at the *exo*-carbon atom not only stabilises the products of the disclosure in anion intermediates of methanofullerenes but also creates an opportunity of their cyclization with the formation of fullerodihydrofurane derivatives.

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References

1 T. Suzuki, Q. Li, K. C. Khemani and F. Wudl, *J. Am. Chem. Soc.*, 1992, **114**, 7301.

2 L. E. Echegoyen, F. D. Djojo, A. Hirsch and L. Echegoyen, *J. Org. Chem.*, 2000, **65**, 4994.

3 R. Kessinger, M. Gowez-Lopez, C. Bondon, J.-P. Gisselbrecht, M. Gross, L. Echegoyen and F. Diederich, *J. Am. Chem. Soc.*, 1998, **120**, 8545.

4 V. V. Yanilkin, V. P. Gubskaya, V. I. Morozov, N. V. Nastapova, V. V. Zverev, E. A. Berdnikov and I. A. Nuretdinov, *Elektrokhimiya*, 2003, **39**, 1285 (*Russ. J. Electrochem*., 2003, **39**, 1147).
5 M. N. J. Benlen, J. E. A. Rivero, M. A. Herranz, A. Martin-Domenich, N. Martin and L. Echegoyen, *Chem. Commun*., 2001, 407.
6 I. A. Nuretdinov, V. V. Yanilkin, V. I. Morozov, V. P. Gubskaya, V. V. Zverev, N. V. Nastapova and G. M. Fazleeva, *Izv. Akad. Nauk, Ser. Khim*., 2002, 250 (*Russ. Chem. Bull., Int. Ed*., 2002, **51**, 263).
7 H. J. Bestmann, C. Moll and C. Bingel, *Synlett*., 1996, 729.
8 M. Ohno, A. Yashiro and S. Eguchi, *Chem. Commun*., 1996, 291.
9 M. N. Nefedova, T. V. Mukha and V. I. Sokolov, *Izv. Akad. Nauk, Ser. Khim*., 1999, 1615 (*Russ. Chem. Bull.*, 1999, **48**, 1594).
10 R. Pellicciari, B. Natalini, T. Potolokova (Mukha), M. Marinozzi, M. Nefedova, A. Peregudov and V. I. Sokolov, *Synth. Commun*., 2003, **33**, 903.

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