72 Russian Chemical Bulletin, International Edition, Vol. 51, No. 1, pp. 72—77, January, 2002

Retro-Bingel reaction in the electrochemical reduction of bis(dialkoxyphosphoryl)methanofullerenes

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

A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan Scientific Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843 2) 75 2253. E-mail: in@iopc.knc.ru

Four steps of reduction were detected for bis(diethoxyphosphoryl)- and bis(diisopropoxyphosphoryl)methano[60]fullerenes (**1**, **2**) and bis(diethoxyphosphoryl)methano[70]fullerene (**3**) by cyclic voltammetry in the *o*-dichlorobenzene—DMF (3 : 1, v/v)/Bu_4NBF_4 (0.1 mol L^{-1}) system on a glass-carbon electrode. At the first step the reversible transfer of one electron affords stable radical anions **1** and **2** (g = 1.9999, ΔH = 1.9 G). When two electrons per molecule are transferred, the methano fragment is rapidly eliminated (retro-Bingel reaction). This process involves the step-by-step cleavage of two C—C bonds of *exo*-carbon with the fullerene shell in combination with the stepwise transfer of other two electrons and a proton to form finally the carbanion of the methano fragment and fullerene dianion. For all studied compounds, the elimination rate is much higher than that for bis(alkoxycarbonyl)- and dialkoxyphosphoryl(alkoxycarbonyl)methano[60]fullerenes, which makes it possible to propose bisphosphorylmethane groups as protective in synthesis of new fullerene derivatives.

Key words: bisphosphorylmethanofullerenes, electrochemical reduction, Bingel reaction, retro-Bingel reaction, radical anion, dianion, elimination of methano fragment, ESR.

The characteristic feature of methanofullerenes with substituents capable of negative charge delocalization is the elimination of the methano fragment accompanied by the transfer of one, two, and more electrons per molecule. Its elimination has first been observed by researchers,[1] who noticed that the radical anions of dicyano- and cyano(ethoxycarbonyl)methano[60]fullerenes undergo fast subsequent transformations and found [60]fullerene in the preparative reduction products. Somewhat later,[2] similar opening of the cyclopropane ring was found for radical anions of spiroannelated methano[60]fullerenes with addends of the quinoid type. However, it seems that the list of compounds in which the methano fragment is eliminated during one-electron reduction is likely restricted by the above examples. Radical anions of other studied methanofullerenes are stable and do not enter into fragmentation reactions. For methanofullerenes obtained in the Bingel reaction,[3] the methano fragment (Bingel addend) is eliminated by the transfer of two and three electrons per molecule.[4—12]

The elimination of the addend from the dianion has first been detected for monosubstituted bis(ethoxycarbonyl)methano[60]fullerene,[4] and the reduction of this adduct at potentials of the second peak followed by oxidation gave [60]fullerene in 60% yield. Although the mechanism of methano fragment elimination from fullerene was not clarified, this process was named the retro-Bingel reaction[4] because the overall interaction gives [60]fullerene. Later methano fragment elimination was observed for the two-electron reduction of the Bingel monoadducts for C_{60}, C_{70}, C_{76}, and C_{78}, the bis- and tris-adducts,[6—8] and in the case of dimethoxyphosphoryl(alkoxycarbonyl)methano[60]fullerenes.[9—11] On going from lowest to highest fullerenes stabilities of the dianions increase and the elimination rates decrease.[7] The chemical variant of the retro-Bingel reaction has recently[12] been performed: elimination of the bis(alkoxycarbonyl)methane addend from C_{60} and C_{70} by magnesium amalgam.

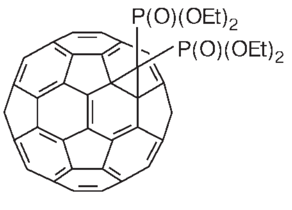
It has been found[13] that the electrochemical reduction of monomethanofullerenes in THF in strictly aprotic media affords bismethanofullerenes, *i.e.*, the methano fragment is transferred from one fullerene shell to another. Dianions of bis- and tris-adducts of C_{60} exhibit, along with the retro-Bingel reaction, intramolecular isomerization *via* addend migration over the fullerene sphere ("walk-on-the-sphere").[6,8] In mixed bis-adducts of C_{60} and C_{70} with the Bingel addend and second addend, which is not prone to anionoid elimination (diarylmethano, [1,2]benzeno fragments, and others), electrolysis at potentials of the second reduction step results in the selective elimination of the Bingel addend to form the monoadduct.[7]

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 70—75, January, 2002.

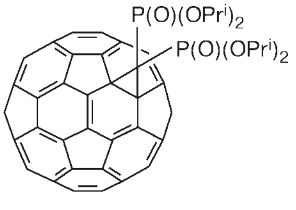
1066-5285/02/5101-72 $27.00 © 2002 Plenum Publishing Corporation

Detailed studies by cyclic voltammetry[9—11] allowed understanding of the mechanism of methano fragment elimination and measurements of the rate constant of this process. According to these data, the elimination of the methano fragment is accompanied by the transfer of two additional electrons and a proton, so that the [60]fullerene dianion and carbanion of the methano fragment are the resulting products. The rate constants for methano fragment elimination are virtually the same for bis(ethoxycarbonyl)- and dimethoxyphosphoryl(alkoxycarbonyl)methano[60]fullerenes. The elimination rate increases substantially for transfer of three electrons per molecule. In this case, diffusion of methanofullerenes to the electrode surface is the limiting stage.

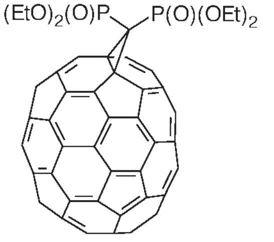
Presently, the methano fragment is considered[7] in the chemistry of fullerenes as a protective group, the introduction of which followed by removal after fullerene functionalization provide some prospects for synthesis of new interesting fullerene derivatives. Successful use of protective groups needs their easy introduction and removal. The nature of substituents at methanocarbon gains a great significance. We have recently* shown that the diphosphorylmethano fragment can much more easily been introduced into the [60]fullerene molecule than the bis(ethoxycarbonyl)methano fragment. In this connection, it is of interest to eliminate this fragment during electrochemical reduction of diphosphorylmethanofullerenes. In this work, we present the results of studying the electrochemical reduction of bis(dialkoxyphosphoryl)methano[60]fullerenes **1**, **2** and bis(diethoxyphosphoryl)methano[70]fullerene (**3**).



1



2



3

Results and Discussion

The cyclic voltammograms for compounds **1—3**, as well as for unsubstituted fullerenes C_{60} and C_{70}, in the *o*-dichlorobenzene—DMF (3 : 1, v/v)/Bu_4NBF_4 (0.1 mol L^{-1}) medium on a glass-carbon electrode exhibit four reduction peaks E_p^{red}, and the reverse branch contain the corresponding four oxidation peaks E_p^{ox} (Fig. 1), whose potentials are presented in Table 1. The ESR spectra are shown in Fig. 2.

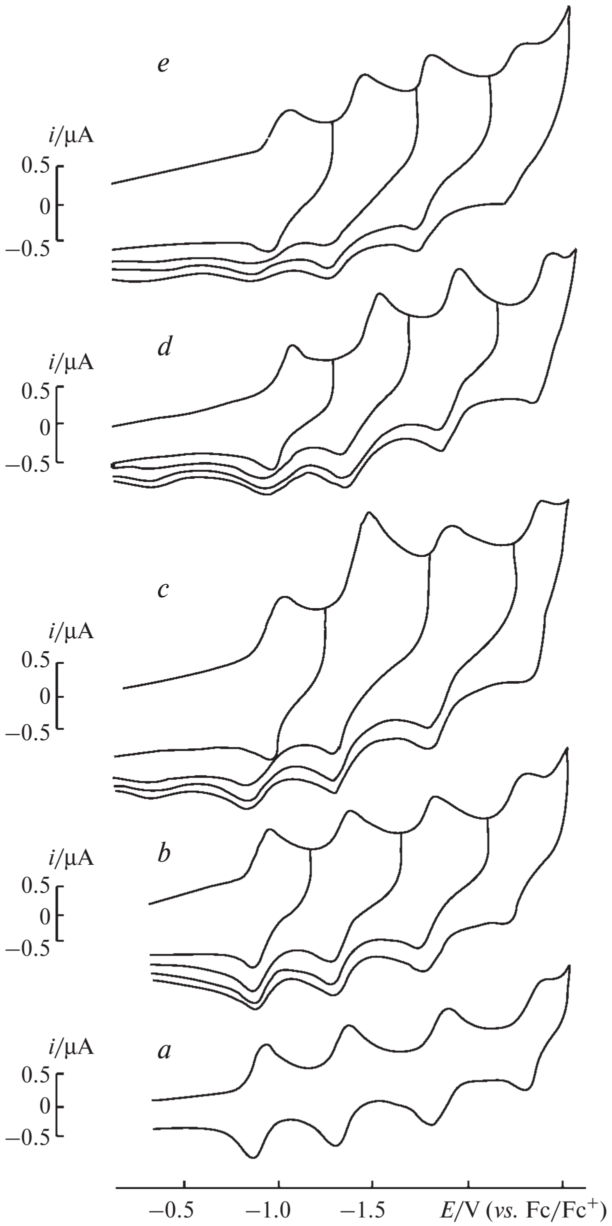


Fig. 1. Cyclic voltammograms for fullerenes C_{60} (*a*), C_{70} (*b*) and compounds **1** (*c*), **2** (*d*), and **3** (*e*) obtained on a glassy-carbon electrode in the *o*-dichlorobenzene—DMF (3 : 1, v/v)/Bu_4NBF_4 (0.1 mol L^{-1}) medium. Conditions: $\upsilon = 100$ mV s^{-1}, $T = 295$ K, $C = 1 \cdot 10^{-3}$ mol L^{-1}.

---

* The results will be published in *Russian Chemical Bulletin, Int. Ed.*, 2002, No. 2.

Table 1. Data of cyclic voltammetry for the reduction of diphosphorylmethanofullerenes **1—3**, C_{60} and C_{70} in *o*-dichlorobenzene—DMF (3 : 1, v/v)/Bu_4NBF_4 (0.1 mol L^{-1}) on a glass-carbon electrode

Compound	E_{p1}^{red}	E_{p1}^{ox}	E_{p2}^{red}	E_{p2}^{ox}	E_{p3}^{red}	E_{p3}^{ox}	E_{p4}^{red}	E_{p4}^{ox}
	V							
C_{60}	−0.96	−0.90	−1.40	−1.33	−1.90	−1.84	−2.39	−2.32
C_{70}	−0.97	−0.91	−1.39	−1.32	−1.84	−1.78	−2.29	−2.22
1	−1.04	−0.98 (−0.90)	−1.49	−1.34	−1.91	−1.84	−2.40	−2.33
2	−1.07	−1.01 (−0.90)	−1.50	−1.34	−1.90	−1.84	−2.39	−2.33
3	−1.07	−1.01 (−0.91)	−1.49	−1.33	−1.83	−1.78	−2.29	−2.22

Note. The potentials (*E*) were measured *vs*. standard potential of the Fc/Fc^+ system using $Ag/AgNO_3$ (0.01 mol L^{-1}) in MeCN as the reference electrode at the potential sweep υ = 100 mV s^{-1}. The potentials of oxidation peaks appeared for potential reverse of the limiting currents of the second, third, and fourth steps of reduction are presented in parentheses.

For fullerenes C_{60} and C_{70} all four steps are reversible and correspond to the stage-by-stage transfer of four electrons per molecule to form tetraanions C_{60}^{4-} and C_{70}^{4-}. The first two reduction peaks of these fullerenes were detected at almost equal potentials, and the third and fourth peaks for C_{70} were observed at less negative potentials, which agrees with published data.[14]

For diphosphorylmethanofullerenes **1—3**, the first two waves are shifted by 80—110 mV toward negative potentials, and the third and fourth steps coincide completely with the potentials of fullerenes C_{60} and C_{70}, respectively. The currents of the first, third, and fourth peaks are equal and correspond to the transfer of one electron per molecule. The height of the second peak depends on the nature of compound and potential sweep but, in all cases, it is higher than the one-electron and lower than the three-electron level (Table 2). The potentials of the second, third, and fourth oxidation peaks also exactly correspond to the oxidation potentials of unsubstituted fullerenes.

The shape and potential of the first oxidation peak depend on the reverse potential and potential sweep. If reverse sweep is performed from potentials of the limiting current of the first peak, then one oxidation peak is observed for compounds **1—3** at all potential sweeps in the interval υ = 20—200 mV s^{-1}. The difference between the potential of this peak and that of the corresponding reduction peak ($\Delta E_{p1} = E_{p1}^{ox} - E_{p1}^{red}$ = 60 mV) is equal to

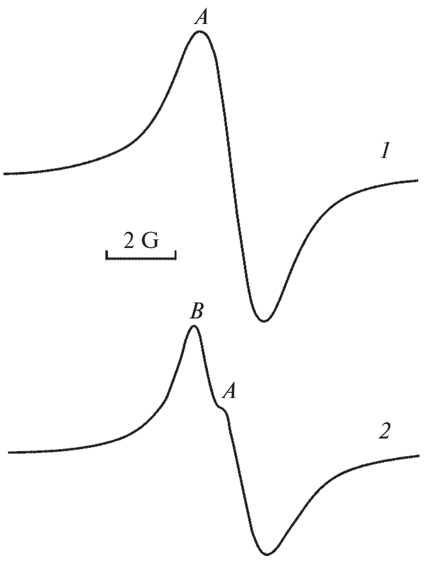


Fig. 2. ESR spectra of paramagnetic intermediates generated by the electrochemical reduction of 10^{-3} *M* solutions of diphosphorylmethanofullerenes **1** (*1*) and **2** (*2*) on a platinum helical electrode in the resonator of the ESR spectrometer at potentials of the first peak in the *o*-dichlorobenzene—DMF (3 : 1, v/v)/Bu_4NBF_4 (0.1 mol L^{-1}) system.

Table 2. Number of transferred electrons (*n*) per molecule of methanofullerenes **1—4** at potentials of the second reduction peak in the *o*-dichlorobenzene—DMF (3 : 1, v/v)/Bu_4NBF_4 (0.1 mol L^{-1}) system and effective rate constants (k_{ef}) for elimination of the methano fragment from dianions **1—4**

Compound	*n* at υ/mV s^{-1}				k_{ef}/s^{-1}
	20	50	100	200	
1	2.23	2.10	1.82	1.70	0.74
2	2.11	1.90	1.75	1.65	0.62
3	1.88	1.83	1.70	1.58	0.53
4*	1.32	1.29	1.25	1.19	0.31

* Published data.[9]

the theoretical value characteristic of reversible processes of one-electron transfer.[15] If the reverse potential sweep is performed from potentials of the limiting current of the second, third, and fourth reduction steps, then the oxidation peak bifurcates, which is especially pronounced at the sweep $\upsilon = 100$ mV s^{-1} (see Fig. 1). One of the appeared peaks corresponds to the oxidation of the radical anions of diphosphorylmethanofullerenes **1—3** ($E_p^{ox} = -0.98$ V (**1**), -1.01 V (**2**, **3**)) and another corresponds to the oxidation of the radical anions of fullerenes C_{60} and C_{70} ($E_p^{ox} = -0.90$ V *vs*. Fc/Fc$^+$).

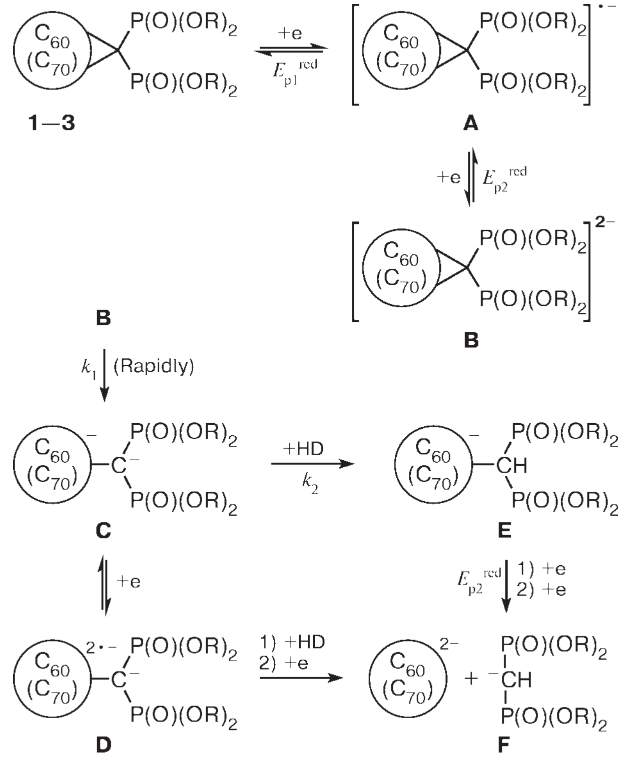
Radical anions of diphosphorylmethano[60]fullerenes **1**, **2** and that of [60]fullerene were detected by ESR. Electrolysis at potentials of the first peak directly in the resonator of the ESR spectrometer allowed us to obtain the spectra of the radical anions of diphosphorylmethano[60]fullerenes **1** and **2** consisting of one line with the *g* factor 1.9999 and line width $\Delta H = 1.9$ G at 295 K (see Fig. 2, curve *1*) and $\Delta H = 1.1$ G at 220 K. Electrolysis of compound **1** is accompanied by the formation of secondary paramagnetic products with $g = 2.0004$, $\Delta H = 0.5$ G and $g = 2.0006$, $\Delta H = 0.3$ G (see Fig. 2, curve *2*), which are usually obtained by the reduction of fullerenes, their derivatives and dimeric fullerene derivatives assigned[16,17] to radical anions. For compound **2**, this product is obtained only after some time of electrolysis. For both diphosphorylmethanofullerenes **1** and **2**, the formation of the radical anion of unsubstituted [60]fullerene was not observed for at least 30 min of electrolysis. The totality of obtained data suggests stability of the radical anions formed by the transfer of one electron to molecules of compounds **1** and **2**.

Electrolysis at potentials of the second reduction peak is accompanied by a decrease in the intensity and the almost complete disappearance of lines of the radical anions and secondary paramagnetic products from the ESR spectra. For the reverse potential sweep, after the oxidation potentials of the dianions are achieved, a broad line of the radical anion of [60]fullerene ($g = 1.999$, $\Delta H \approx 70$ G) appears and its intensity increases, whereas reverse at the oxidation potentials of the radical anions results in a decrease in the intensity and entire disappearance of this line.

Thus, the data obtained by two methods show that the radical anions of diphosphorylmethanofullerenes **1** and **2** generated by electrochemical reduction at potentials of the first wave are stable in *o*-dichlorobenzene—DMF (3 : 1, v/v), enter into reversible coupling reactions with the initial molecule but do not eliminate the methano fragment for at least 30 min. Based on the complete analogy of the cyclic voltammograms of compounds **1** and **2**, on the one hand, and compound **3**, on the other hand, we can assume high stability and similar transformations of radical anions of diphosphorylmethano[70]fullerene **3**.

Transfer of two electrons to molecules of compounds **1—3** to form the dianion results in the elimination of the methano fragment. Coincidence of the third and fourth reduction peaks, the second, third, and fourth oxidation peaks with the corresponding peaks for C_{60} and C_{70} and the one-electron level of the third and fourth reduction peaks unambiguously indicate that compounds **1—3** eliminate the methano fragment with the diffusion rate in almost 100% yield at potentials of the second step. This elimination is much slower in the case of bis(alkoxycarbonyl)- and dialkoxyphosphoryl(alkoxycarbonyl)methano[60]fullerenes and is accompanied by the transfer of additional two electrons and a proton to the methano fragment.[4,9—11] It is most likely that the process occurs similarly in the case of studied diphosphorylmethanofullerenes **1—3**, whose reduction at potentials of the first two waves can be described by Scheme 1.

Scheme 1



R is alkyl

Radical anion **A**, formed by heterogeneous reduction on the electrode at the first wave potentials, is transformed into dianion **B** at the second wave potentials. In dianion **B** the C—C bond is cleaved and the cyclopropane rings opens to form dianion **C**, which finally affords dianions of fullerenes C_{60}^{2-}, C_{70}^{2-} and diphosphorylmethanocarbanion **F** through parallel processes of methanocarbon protonation and reduction to radical trianion **D** (see Scheme 1). The oxidation peak in the cyclic curves at the potential near -0.20 V corresponds, most likely, to the oxidation of anion **F** (see Fig. 1). During the reduction of bis(alkoxycarbonyl)- and dialkoxyphosphoryl(alkoxycarbonyl)methano[60]fullerenes,[9—11] dianions of fullerenes $C_{60}{}^{2-}$, $C_{70}{}^{2-}$, as well as radical trianion $C_{60}{}^{\bullet 3-}$, can participate in the homogeneous reduction of compounds **1—3** and their radical anions **A** (Scheme 2).

Scheme 2

$$C_{60}(C_{70})^{2-} + \mathbf{1{-}3} \rightleftharpoons C_{60}(C_{70})^{\bullet -} + \mathbf{A},$$

$$C_{60}(C_{70})^{2-} + \mathbf{A} \rightleftharpoons C_{60}(C_{70})^{\bullet -} + \mathbf{B}.$$

As mentioned above, for all diphosphorylmethanofullerenes **1—3** the methano fragment is eliminated in almost 100% yield at potentials of the second wave. This implies that the rate of cyclopropane ring opening (k_1) is equal to or higher than the diffusion rate of compounds **1—3** to the electrode surface. In the opposite case, *i.e.*, if the rate of this stage would be lower than the diffusion rate, the height of the third peak should exceed the one-electron level. If all subsequent stages in Scheme 1 occur with the diffusion rate at potentials of the second peak or at less negative potentials, the height of the second peak would correspond to the three-electron level. The number of electrons, which really does not exceed three, depends on the nature of diphosphorylmethanofullerene **1—3**, and increases with a decrease in the potential sweep (see Table 2). Evidently, one or several stages of Scheme 1 are delayed.

Using compound **3**, we showed that the introduction of a tenfold amount of the proton donor (phenol) increases the heights of the second and third peaks and the appearance of an additional cathodic peaks (Fig. 3). At the same time, phenol additives have no effect on the first two stages of reduction of unsubstituted fullerene C_{70} (see Fig. 3). This implies that the radical anion and dianion of C_{70} are not protonated within the time of recording cyclic voltammograms. Only radical trianions are efficiently protonated to form hydrofullerenes, whose reduction is observed as an additional wave. It is likely that radical anions **A** and dianions **B** of diphosphorylmethano[70]fullerene **3** are not either protonated by phenol under conditions of cyclic voltammetry. In this case, the current increase of the second peak in the presence of phenol is a result of an increase in the contribution of the decelerated stage of protonation of dianion **C**. Evidently, dianion **C** is reduced at potentials of the second step, although somewhat less easily than anion **E** and radical anion **A**. Under conditions of polarography or a rotating disk electrode, this difference in reduction potentials would not reflect the limiting current value and it would correspond the three-electron level; however, under conditions of cyclic voltammetry this results in a decrease in the peak current.

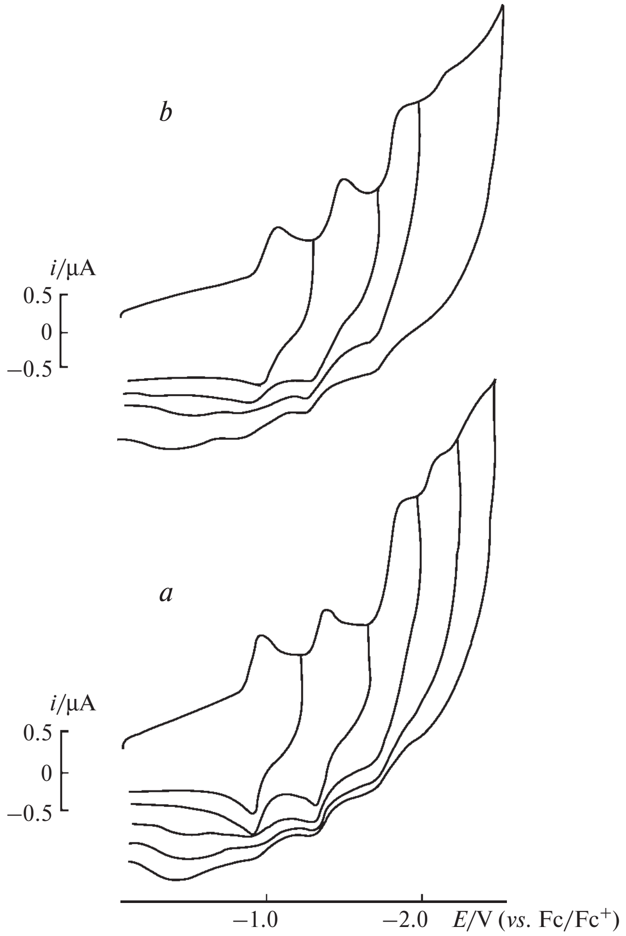


Fig. 3. Cyclic voltammograms for fullerene C_{70} (*a*) and compound **3** (*b*) obtained on a glass-carbon electrode in *o*-dichlorobenzene—DMF (3 : 1, v/v)/Bu_4NBF_4 (0.1 mol L^{-1}) in the presence of phenol (0.01 mol L^{-1}). Conditions: $\upsilon = 100$ mV s^{-1}, $T = 295$ K, $C = 1 \cdot 10^{-3}$ mol L^{-1}.

Previously,[9—11] based on the height of the second reduction wave, we calculated the elimination rate constant for the methano fragment from bis(diethoxycarbonyl)- and dimethoxyphosphoryl(alkoxycarbonyl)methano[60]fullerenes. Similarly, using the Nicholson method,[18] we determined the effective rate constant for addend elimination from the dianions of diphosphorylmethanofullerenes **1—3** (see Table 2). The corresponding values for bis(diethoxycarbonyl)methano[60]fullerene **4** are presented for comparison.[9] As can be seen, the effective elimination rate constant (k_{ef}) for the diphosphorylmethano addends from C_{60} and C_{70} is much higher than that for the classical Bingel addend. It is noteworthy that the diphosphorylmethano addends, as well as the Bingel addend,[7] eliminate from C_{60} more readily than from C_{70}.

Thus, the electrochemical reduction of diphosphorylmethanofullerenes **1—3** is similar to the reduction of other previously studied bis(diethoxycarbonyl)- and dimethoxyphosphoryl(alkoxycarbonyl)methano[60]fullerenes[4—11] with the only distinction that, in this case, the processes of methano fragment elimination occur with a high rate at the stage of the dianion. In other words, the diphosphorylmethano fragment is the best leaving group in electron transfer compared to the ethoxyphosphoryl(ethoxycarbonyl)- and bis(ethoxycarbonyl)methane fragments. The presence of two diethoxyphosphoryl groups enhances both nucleophilicity and nucleophobicity of the methano fragment. This group can easily be introduced into the reaction and, therefore, the use of it as protective in fullerene functionalization seems preferential.

Experimental

C_{60} and C_{70} with purity (HPLC data) 99.5 and 98%, respectively, a Gilson chromatograph with a UV detector, and a column with the reverse C_{18} phase (Partisil-5 ODS-3) and toluene—MeCN, 1 : 1, v/v, as eluent were used. Organic solvents were dried and distilled. Procedures for synthesis and physicochemical characteristics of diphosphorylmethanofullerenes **1—3** will be published elsewhere (see Footnote in p. 72). Electrochemical reduction of C_{60}, C_{70} and diphosphorylmethanofullerenes **1—3** was conducted in the *o*-dichlorobenzene—DMF (3 : 1, v/v) medium. Bu_4NBF_4 (0.1 mol L^{-1}) purified by recrystallization from acetonitrile was used as supporting electrolyte. Cyclic voltammograms were detected with an PI-50-1 potentiostat on an N-307/2 two-coordinate recorder. A glass-carbon disk electrode (d = 2 mm) embedded into Teflon served as working electrode. Before each measurement, electrodes were mechanically polished. Potentials were measured *vs.* standard potential of the ferrocene/ferrocenium ion (Fc/Fc^+) redox system using a silver reference electrode $Ag/AgNO_3$ (0.01 mol L^{-1}) in MeCN. Dissolved oxygen was removed by bubbling argon or nitrogen through a solution at 295 K.

The study by the electrolysis—ESR method was performed on an installation combining an SE/X-2544 ESR spectrometer, a PI-50-1 potentiostat, and an electrochemical cell. The installation allows one to carry out an electrochemical process directly in the resonator of the ESR spectrometer. A platinum coil served as working electrode, a platinum wire was the auxiliary electrode, and a silver wire served as reference electrode. Solutions were degassed by the triply repeated cycle of freezing—evacuation—thawing out. The temperature was 295 K.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 99-03-32888 and 01-03-32181), State Scientific Technical Program "Fullerenes and Atomic Clusters" (Project No. 98008 "Gemo-2"), and Academy of Sciences of Tatarstan.

References

1. K. M. Keshavarz, B. Knight, R. C. Haddon, and F. Wudl, *Tetrahedron*, 1996, **52**, 5149.
2. B. Knight, N. Martin, T. Ohno, E. Orti, C. Rovira, J. Veciana, J. Vidol-Gancedo, P. Viruela, R. Viruela, and F. Wudl, *J. Am. Chem. Soc.*, 1997, **119**, 9871.
3. C. Bingel, *Chem. Ber.*, 1993, **126**, 1957.
4. R. Kessinger, J. Crassons, A. Herrmann, M. Ruttimann, L. Echengoyen, and F. Diederich, *Angew. Chem.*, 1998, **110**, 2022.
5. C. Boudon, J.-P. Gisselbrecht, M. Gross, A. Hermann, M. Ruttiman, J. Crassons, F. Cardullo, L. Echegoyen, and F. Diderich, *J. Am. Chem. Soc.*, 1998, **120**, 7860.
6. L. E. Echegoyen, F. D. Djojo, A. Hirsch, and L. Echegoyen, *J. Org. Chem.*, 2000, **65**, 4994.
7. R. Kessinger, N. S. Fender, L. E. Echegoyen, C. Thilgen, L. Echegoyen, and F. Diederich, *Chemistry*, 2000, **6**, 2184.
8. R. Kessinger, M. Gowez-Lopez, C. Bondon, J.-P. Gisselbrecht, M. Gross, L. Echegoyen, and F. Diederich, *J. Am. Chem. Soc.*, 1998, **120**, 8545.
9. I. A. Nuretdinov, V. V. Yanilkin, V. P. Gubskaya, N. I. Maksimyuk, and L. Sh. Berezhnaya, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 426 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 427].
10. V. V. Yanilkin, I. A. Nuretdinov, V. P. Gubskaya, N. I. Maksimyuk, N. V. Nastapova, L. Sh. Berezhnaya, and V. I. Morozov, *7th Intern. Frumkin Symposium (Moscow, 23—28 October, 2000)*, *Abstrs.*, Moscow, 2000, 405.
11. I. A. Nuretdinov, V. P. Gubskaya, L. Sh. Berezhnaya, G. M. Fazleeva, V. V. Yanilkin, V. V. Zverev, V. I. Morozov, F. G. Sibgatullina, and I. P. Karaseva, *Mezhdun. konf. "Metalloorganicheskie soedineniya — materialy budushchego tysyacheletiya»" (III Razuvaevskie chteniya)* [*Intern. Conf. Organometallic Compounds as Materials of Next Millenium (III Razuvaev´s Readings*] (*May 29—June 2, 2000*), *Abstrs.*, Nizhnii Novgorod, 2000, 110 (in Russian).
12. N. N. P. Moonen, C. Thilgen, L. Echegoyen, and F. Diederich, *Chem. Commun.*, 2000, 335.
13. M. N. J. Benlen, J. E. A. Rivero, M. A. Herranz, A. Martin-Domenich, N. Martin, and L. Echengoen, *Chem. Commun.*, 2001, 407.
14. D. Dubois, K. M. Kadish, S. Flanagan, R. E. Haufler, L. P. F. Chibante, and L. J. Wilson, *J. Am. Chem. Soc.*, 1991, **113**, 4364.
15. Z. Galus, *Teoretyczne podstawy electroanalizy cheicznei* [*Theoretical Foundations of Electroanalysis*], Panstwowe wydawnicctwo naukowa, Warszawa, 1971 (in Polish).
16. V. Brezova, A. Stasko, P. Rapta, D. M. Guldi, K.-D. Asmus, and K.-P. Dinse, *Magn. Reson. Chem.*, 1997, **35**, 795.
17. P. Paul, R. D. Bolskar, A. M. Clark, and C. A. Reed, *Chem. Commun.*, 2000, 1229.
18. R. S. Nicholson and J. Shain, *Anal. Chem.*, 1965, **37**, 190.

Received June 20, 2001