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Phosphorylated methano[60]fullerenes containing nitroxyl radicals: synthesis, structures, and electrochemical behavior

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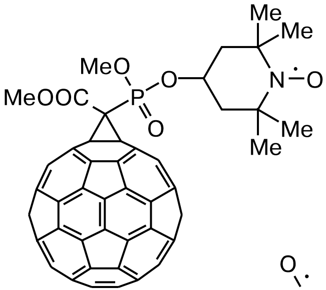
Phosphorylated methano[60]fullerenes containing one or two nitroxyl radicals were synthesized for the first time. Their structures were established from spectroscopic data and their compositions, by MALDI-TOF mass spectrometry. Their electrochemical reduction in a system *o*-dichlorobenzene—DMF/0.1 *M* Bu_4NBF_4 was studied by cyclic voltammetry, preparative electrolysis, and ESR spectroscopy in combination with *in situ* electrolysis. Both compounds were found to undergo four-step reduction of the fullerene sphere, reduction of nitroxyl, opening of the three-membered ring, and elimination of addends as carbanions stabilized by protonation and rearrangement into phosphate ions and substituted acetylene, which are accompanied by the formation of free fullerene and dihydrofuranofullerene. The rates of the ring opening and the addend elimination increased with an increase in the negative charge on the fullerene sphere. These reactions are fast in the case of transfer of three electrons. With the use of model compounds, heterogeneous electron transfer to the nitroxyl radical at the potentials of the transfer of the third electron to the fullerene sphere and homogeneous intramolecular electron transfer from the dianion of the fullerene sphere were revealed. The mechanisms of the observed transformations are discussed.

Key words: 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl, phosphorylated methanofullerene, electrochemical reduction, electron transfer, ESR spectroscopy, ring opening, elimination of the addend, the Bingel retroreaction.

Compounds containing stable radicals are of interest as spin-labeled biologically active compounds and traps for radicals in living systems.[1,2] In the chemistry of fullerenes, nitroxyl-containing mono- and bisadducts of the [60]fullerenopyrrolidine and methano[60]fullerene types have been documented and their structures and properties have been studied by the ESR method.[3—6] It was shown[7,8] that incorporation of nitroxyl radicals into certain phosphorylated alkylating antitumor preparations makes them less toxic for warm-blooded animals and increases their antitumor efficiency. Recently,[9] phosphorylated methano[60]fullerenes have been found to be an order of magnitude more efficient as traps for free radicals than unsubstituted fullerene C_{60}, the reactive site being the fullerene sphere. A combination in one molecule of methanofullerene, phosphonate, and nitroxyl radical fragments with inherent properties is promising for design of new biologically active compounds. In the present work, we describe the synthesis of, and electron transfer processes in, novel phosphorylated methanofullerenes **1** and **2** containing these functional groups.



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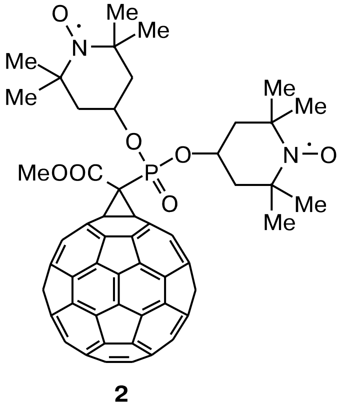

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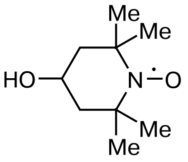
Results and Discussion

Synthesis and structure. Compounds **1** and **2** were obtained by the reactions of fullerene C_{60} with the corresponding nitroxyl-containing alkyl phosphorylacetates prepared from 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (**3**) and phosphorylacetyl chlorides as described earlier.[10,11]



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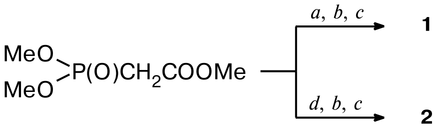
The formation of the corresponding nitroxyl-containing methanofullerenes **1** and **2** occurs in the presence of tetrabromomethane and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Scheme 1).

Scheme 1



Reagents: *a*. $POCl_3$; *b*. radical **3**, Et_3N; *c*. C_{60}, CBr_4, DBU; *d*. PCl_5.

Compounds obtained were isolated by column chromatography on SiO_2. Their structures were established by spectroscopy and their compositions, by MALDI-TOF mass spectrometry.

The UV spectra of compounds **1** and **2** show absorption bands at 258, 326, 427.9, and 492 nm for the fullerene cage, which preclude observation of an absorption band of the nitroxyl group at 459 nm. The absorption band at 428 nm is characteristic of monomethanofullerenes, in which the methano fragment is attached to the 6,6-bond of the fullerene sphere.

The IR spectra of these compounds contain an absorption band at 527 cm^{-1} typical of vibrations of the fullerene bonds, as well as at 1740 (C=O), 1000 and 1046 (P—O—C), and ~1235 cm^{-1} (P=O).

The ^1H NMR spectra of compounds **1** and **2** are not informative because signals for all protons are paramagnetically broadened due to the presence of the nitroxyl fragment. However, the ^{13}C NMR spectra contain distinct signals for the sp^2-hybridized C atoms of the fullerene cage at δ 136—160, which are virtually the same for both compounds, and for the sp^3-hybridized C atoms at δ 68—69. Weak broadened signals for the C(61) atom of the methane fragment appear at δ 54.

Molecular ion peaks with *m/z* 1042.275 and 1182.850 in the MALDI-TOF mass spectra of methanofullerenes **1** and **2**, respectively, confirm their compositions. In addition, the mass spectra of these compounds contain peaks of fragmentation ions produced upon abstraction of the nitroxyl fragment from the initial molecules. For instance, the mass spectrum of methanofullerene **1** shows a peak with *m/z* 887.883 corresponding to the abstraction of one nitroxyl fragment, while the mass spectrum of compound **2** shows peaks with *m/z* 1028.969 and 872.736 corresponding to the abstraction of one and two nitroxyl fragments from the P atom with retention of the methoxy group.

The presence of the nitroxyl fragments in compounds **1** and **2** was also confirmed by ESR spectroscopy. In the solid state, radicals **1**, **2**, and **3** are characterized by singlet lines with an integral intensity ratio of 1 : 2 : 1 and line widths of 1.9, 1.8, and 0.9 mT, respectively. Exchange interactions are stronger for the more magnetically concentrated compound **3**, while the biradical nature of compound **2** does not manifest itself in a room-temperature spectrum. The ESR spectrum of radical **3** in toluene (Fig. 1) at 233 K agrees with the literature data:[12,13] $g = 2.0062$, $a_N = 1.56$ mT, $a_{2H} = 0.049$ mT, $a_{6H} = 0.045$ mT, and $a_{2H} = 0.037$ mT. Hyperfine couplings with the N nucleus of the nitroxyl fragment and with the protons of two axial methyl groups and two methylene groups of the ring are observed. For radicals **1** and **2** (solutions in toluene), such a proton 11-line hyperfine structure (HFS) is retained in the ESR spectra (see Fig. 1), as has been noted earlier for other mono- and biradical products containing 2,2,6,6-tetramethylpiperidine 1-oxyl radical.[12,13] Because the conformational composition is complicated and the exchange is retarded resulting in line broadening, the HFS is partially collapsed giving partially resolved multiplet spectra with $\langle a_H \rangle \approx 0.039$ mT. For biradical compound **2**, the observed components due to strong exchange in the biradical system with $|J_{eff}/a_N| = 2.6$ (295 K) suggest a retarded conformation-dependent electron exchange.

Cyclic voltammetry (CV). Electrochemical reduction (ER) of compounds **1** and **2** with a glassy carbon electrode in *o*-dichlorobenzene—DMF (3 : 1, v/v)/0.1 *M* Bu_4NBF_4 proceeds in several steps (Table 1). The

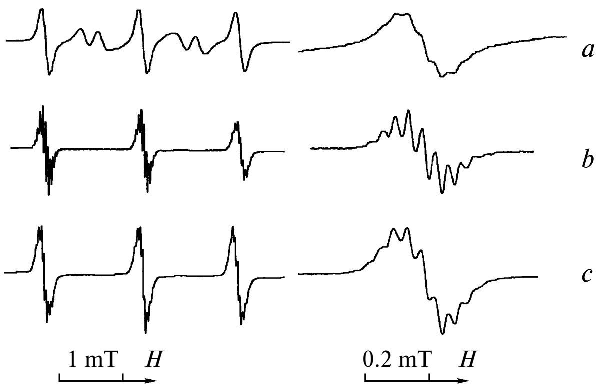


Fig. 1. ESR spectrum of methanofullerenes **2** (*a*) and **1** (*b*) and radical **3** (*c*) in toluene; $C = 1 \cdot 10^{-3}$ mol L^{-1}, $T = 295$ K.

Table 1. CV data for the reduction of C_{60}, methanofullerenes **1**, **2**, and **4**, and nitroxyl radical **3** in *o*-dichlorobenzene—DMF (3 : 1, v/v)/0.1 *M* Bu_4NBF_4 on a glassy carbon electrode[a]

Compound	$-E_{p,(C_1)}$	$-E_{p,(A_1)}$, $(-E_{p,(A_1')})$	$-E_{p,(C_2)}$	$-E_{p,(A_2)}$, $(-E_{p,(A_2')})$	$-E_{p,(C_3)}$	$-E_{p,(C_4)}$	$-E_{p,(A_4)}$	$-E_{p,(C_5)}$	$-E_{p,(C_6)}$	$-E_{p,(A_6)}$	$-E_{p,(A_0)}$	E_p^{ox} [b]
C_{60}[c]	0.96	0.90	1.40	1.33	1.90	2.39	2.32	—	—	—	—	—
1	0.99	0.93 (1.00)[d]	1.43	1.36 (1.34)[d]	1.66	1.95	1.84	2.12	2.40	2.33	0.48	0.27
2	0.99	0.93 (0.96)[d]	1.45	1.37 (1.34)[d]	1.66	1.97	1.85	2.15	2.40	2.30	0.48	0.27
3	1.95	1.02	—	—	—	—	—	—	—	—	—	0.27
4[e]	1.02	0.96 (1.04)[d]	1.45	1.39 (1.36)[d]	1.66	1.95	1.85	2.14	2.40	2.33	0.48	—

[a] Potentials (V) were measured with respect to a standard potential of the Fc/Fc^+ redox system using Ag/0.01 *M* $AgNO_3$ in MeCN as a reference electrode at the scan rate υ = 20 mV s^{-1}.

[b] For methanofullerenes **1** and **2** and radical **3**, a reversible oxidation peak at E_p^{ox} = 0.27 V appears in the anodic potential range.

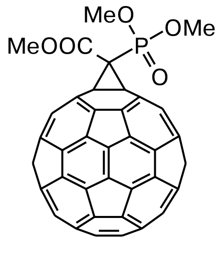
[c] $E_{p,(A_3)} = -1.84$ V.

[d] The potentials of the oxidation peaks detected on the reverse scan of potential from the third and next reduction peaks are given in parentheses.

[e] $E_{p,(A_5)} = 2.08$ V.

CV curves at the potential scan rates υ = 20, 50, and 100 mV s^{-1} contain four main reduction peaks C_1, C_2, C_4, and C_6 corresponding to electron transfer to the fullerene sphere and the four respective reoxidation peaks A_1, A_2, A_4, and A_6. In addition, two more reduction peaks C_3 and C_5 are observed, which have intensities virtually independent of the nature of the compound. Peak C_3 is weak at all scan rates, while the height of peak C_5 is appreciably sensitive to the scan rate. The number and potentials of the reduction and reoxidation peaks are virtually the same for both compounds. With a decrease in υ from 100 to 20 mV s^{-1}, the relative intensities of the peaks C_5 become lower as compared with the main peaks. At 20 mV s^{-1}, these peaks are faintly discernible, although they are well pronounced at 100 mV s^{-1} (Fig. 2). This indicates that the ER products of nitroxyl-containing methanofullerenes **1** and **2** at the potentials of peaks C_3 and C_5 yield electrochemically inert compounds in this potential range. The difference between the potentials of peaks C_3 and C_5 is ~0.50 V, which allows these peaks to be attributed to the stepwise reduction of the same new fullerene intermediate generated during the ER of the starting methanofullerenes.

The potentials of the sixth peaks C_6 of methanofullerenes **1** and **2** are exactly the same as the potential of the fourth reduction peak for C_{60}, *i.e.*, of the reversible process $C_{60}{}^{3-} + e^- \rightleftharpoons C_{60}{}^{4-}$ (see Table 1). The reduction peaks C_1, C_2, and C_4 appear at lower potentials than the corresponding peaks in the reduction of fullerene C_{60} (by 30, 30—40, and 50—100 mV, respectively). This agrees with our previous[14—16] data on the reduction of (methoxycarbonyl)dimethoxyphosphorylmethano[60]fullerene **4** in $PhCH_3$—DMF (2 : 1)/0.1 *M* Et_4NBF_4 and is in conflict with data[17] on the reduction of (ethoxycarbonyl)diethoxyphosphorylmethano[60]fullerene in CH_2Cl_2/0.1 *M* Bu_4NPF_6 where easier reduction of methanofullerene was reported.



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The current of the first reduction peak C_1 for each of compounds **1** and **2** corresponds to single-electron transfer per depolarizer molecule; the heights of the second and fourth peaks C_2 and C_4 substantially exceed the one-electron level. Qualitatively, one can note that the heights of peaks C_1, C_2, C_3, and C_5 for biradical **2** are virtually the same as those for monoradical **1**, but the currents of the fourth and sixth peaks C_4 and C_6 are significantly higher.

The morphologies of the reoxidation voltammograms are identical for both compounds and depend on the switching potential. On the reverse scan directly from the potential E_1 of the first reduction peak, a reoxidation peak A_1 appears at $E_{p,(A_1)} = -0.93$ V, *i.e.*, its potential is shifted by 60 mV in the anodic direction as compared with the reduction peak C_1. This suggests that single-electron reversible reduction at the potential of the first peak C_1 yields stable fullerene-centered radical anions (RA). Taking into account that the substituents contain nitroxyl radicals as well, these species will be biradical anions in the case of compound **1** and triradical anions in the case of compound **2**. The reverse scan from the potential E_2 of the second reduction peak revealed two oxidation peaks A_1 and A_2; the low intensity of the peak A_2 ($E_{p,(A_2)}$ = −1.36 V) corresponding to the oxidation of fullerene-centered dianions of compounds **1** and **2** suggests that the dianions are involved in chemical reactions. At the more

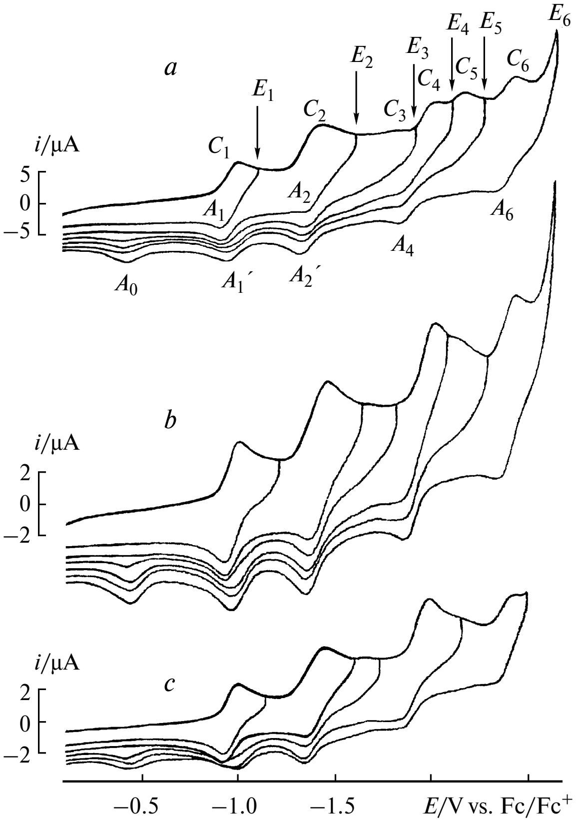


Fig. 2. Cyclic voltammograms of methanofullerene **1** ($C = 1 \cdot 10^{-3}$ mol L^{-1}) recorded with a glassy carbon electrode in *o*-dichlorobenzene—DMF (3 : 1, v/v)/Bu_4NBF_4 (C = 0.1 mol L^{-1}) at different scan rates: 100 (*a*), 50 (*b*), and 20 mV s^{-1} (*c*); T = 295 K.

negative switching potentials E_3, E_4, E_5, and E_6, the peak A_2 increases and its potential becomes somewhat less negative and equals, in the limit, the oxidation potential of the fullerene C_{60} dianion to RA ($E_{p,(A_2')} = -1.34$ V). This is accompanied by broadening of the first reoxidation peak A_1 and its shift to negative values ($E_{p,(A_1')} = -0.96$ V). An additional reoxidation peak A_0 appeared on the reverse scan from the potential E_3 ($E_{p,(A_0)} = -0.48$ V). The height of this peak increases with a decrease in the switching potential. No anodic peaks were detected at the potentials of the peaks C_3 and C_5, which suggests their irreversibility. The fourth reduction peak C_4 is also irreversible. However, on the reverse scan from the more negative potentials E_5 and E_6, an anodic peak A_4 appeared at the potential of oxidation of fullerene radical trianions $C_{60}{}^{\bullet 3-}$ into dianions $C_{60}{}^{2-}$ ($E_{p,(A_4)} = -1.84$ V). The reduction at the potential of the sixth peak revealed an anodic peak due to oxidation of fullerene tetraanions $C_{60}{}^{4-}$ into radical trianion $C_{60}{}^{\bullet 3-}$ (A_6 at $E_{p,(A_6)} = -2.33$ V).

Earlier,[4—6] it has been found that the CV curves (THF, 0.05 M Bu_4NPF_6 as a supporting electrolyte, a Pt electrode) of methanofullerenes and fullerenopyrrolidines containing 2,2,6,6-tetramethylpiperidine 1-oxyl as a substituent at carbon C(61) or in the pyrrolidine ring show five reversible reduction peaks of the fullerene sphere and an irreversible peak of the nitroxyl radical reduction, which is between the second and third reduction peaks of the fullerene sphere. For nitroxyl-containing fullerenopyrrolidines, the reduction potentials of the fullerene sphere equal those for other fullerenopyrrolidines. All the aforementioned facts suggest that fullerene and nitroxyl are reduced independently and do not interact with each other. Only electron transfer processes are characteristic of these compounds, anionic intermediates being stable. Neither the radical anions nor dianions of the methanofullerene and fullerenopyrrolidine frameworks reduce the nitroxyl radical in the intra- and intermolecular manner; *i.e.*, the electrochemical reduction of nitroxyl is not mediated by the fullerene sphere.

For compounds **1** and **2**, the reduction pattern is complicated by opening of the three-membered ring and elimination of the addend. Such methanofullerenes containing dialkoxyphosphoryl and alkoxycarbonyl groups at the C(61) atom were investigated earlier in toluene—DMF (2 : 1)/0.1 M Et_4NBF_4 [14—16] and CH_2Cl_2/0.1 M Bu_4NPF_6.[17] In these media, radical anions were stable, while more negatively charged intermediates lost the addend. The difference was that the elimination in toluene—DMF partially occurred at the second reduction step (during the formation of a dianion) and quantitatively at the third step (during the formation of a radical trianion), while in CH_2Cl_2, this process took place only during the generation of a radical trianion. In the present study, ER of methanofullerenes **1** and **2** was carried out in a different medium, *viz.* *o*-dichlorobenzene—DMF (3 : 1, v/v)/0.1 M Bu_4NBF_4. For this reason, the previous ER data for such methanofullerenes cannot directly be used to interpret our data obtained for compounds **1** and **2** since the medium is obviously substantial in stabilization of intermediates. Nevertheless, based on known literature data[14—18] and taking into account that the potentials of the reduction peak C_6 and the reoxidation peaks A_2', A_4, and A_6 equal the corresponding reduction and reoxidation peaks for fullerene C_{60}, one can assume that elimination of the addends (the Bingel retroreaction) occurs during the ER at the potentials of peaks C_2—C_5.

As with other methanofullerenes containing electron-withdrawing substituents,[14—17,19—28] elimination begins with opening of the three-membered ring. Ring opening often results in elimination of the addend but sometimes in its migration along the fullerene sphere[22,24] or its transfer to the fullerene sphere of another molecule to give bismethanofullerenes[26] and dimeric intermediates with a single bond between the fullerene spheres.[17] Carbonyl-containing methanofullerenes yield fullerenodihydrofurans.[29,30] In principle, all these transformations are possible in the reduction of methanofullerenes **1** and **2**.

A peak analogous to peak C_5 was observed[17] in the ER of ethoxycarbonyl(diethoxyphosphoryl)methano[60]fullerene in CH_2Cl_2 and assigned to the addend reduction. Even if electron transfer to the addends followed by opening of the three-membered ring at the potentials of peak C_5 and in the reduction of compounds **1** and **2** seems to be highly probable, the available data do not allow us to rule out the possible reduction of anionic fullerene intermediates with the opened three-membered ring at the potentials of peaks C_3 and C_5.

Thus, the ER of compounds **1** and **2** at potentials below −2.5 V involves four-step reduction of the fullerene sphere, elimination of the addends, and irreversible electron transfer to nitroxyl. Cyclic voltammograms and literature data allow unambiguous interpretation of only the first reduction step. It remains absolutely unclear what processes occur at more negative potentials and in what sequence they appear. To obtain a more comprehensive picture of the reduction, we performed an ER study of compounds **1** and **2** by ESR spectroscopy in combination with *in situ* electrolysis. We carried out preparative reduction of compound **1** and analyzed the reaction mixture using ^{31}P NMR spectroscopy and chromatography; in addition, we studied the electrochemical behavior of the model compounds methanofullerene **4** and nitroxyl radical **3** and their 1 : 1 and 1 : 2 mixtures.

ESR study in combination with *in situ* electrolysis. The electrochemical reduction of methanofullerene **4** at the potentials of the first peak gave a stable RA with $g = 1.9999$ and the line width $\Delta H = 0.21$ mT (313 K).

The reduction of radical **3** at −1.95 V was accompanied by the loss of its paramagnetism, which was slowly but fully restored upon the reoxidation at −0.5 V. The reduction of a 2 : 1 mixture of compounds **3** and **4** proceeded analogously to the reduction of individual compounds **3** and **4** (Fig. 3); however, in this case, the slow reduction of the nitroxyl fragment began at the potential of second peak C_2 during the ER of methanofullerene **4**.

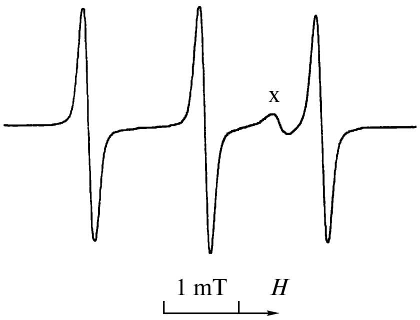


Fig. 3. ESR spectrum of a solution of a mixture of methanofullerene **4** ($C = 1 \cdot 10^{-3}$ mol L^{-1}) and radical **3** ($C = 2 \cdot 10^{-3}$ mol L^{-1}) in *o*-dichlorobenzene—DMF (3 : 1, v/v)/Bu_4NBF_4 ($C = 0.1$ mol L^{-1}) in the reduction at the potential of the first peak C_1; x refers to the radical anion of methanofullerene **4**.

The nitroxyl radical disappeared upon prolonged electrolysis at the potential of the fourth peak C_4 and was completely regenerated in the reoxidation at the potentials of A_1'. In this case, the primary radical anion of methanofullerene is somewhat less stable than in the absence of radical **3**.

The electrochemical reduction of methanofullerene **1** at the potential of the first peak (313 K) was accompanied by a sharp decrease in the intensity of the ESR signal for the nitroxyl radical of the starting reagent. The resulting spectrum (Fig. 4) is characterized by half the HFC constant with the nitrogen nucleus and the *g* factor average of the *g* factors of the nitroxyl radical and the RA of methanofullerene, as for nitroxyl-containing methanofullerenes and fullerenopyrrolidines studied earlier.[5,6] The exchange is conformation-dependent to a large extent, for which reason the experiment was carried out at 313 K. At lower temperatures, the lines of the ESR spectrum became much broader.

Electrolysis at the potential of the second peak was accompanied by a sharp increase in the intensity of the signal for the nitroxyl radical because of the diamagnetism of methanofullerene dianions followed by its slow decline. At the potential of the fourth peak C_4, rapid quenching of the signal for the nitroxyl radical occurs, which recovers upon the oxidation at the potentials of the first peak. The multiplet for the protons became more resolved and a_N increased from 1.56 to 1.57 mT (see Fig. 4), probably because of opening of the three-membered ring and elimination of the addend (Scheme 2). This new nitroxyl radical in the free addend, which is not attached to the fullerene sphere, was also obtained upon preparative electroreduction at the potential of peak C_4 and reoxidation at −0.5 V (Fig. 5).

As with methanofullerene **1**, the electrochemical reduction of methanofullerene biradical **2** at the potential of the first peak (313 K) was accompanied by disappearance of the primary signal for the biradical and the formation of a triradical anion system with $g = (2g_{N-O} + g_{C_{60}})/3 = 2.0040$ and $a_N = 2a_{N-O}/3 = 1.03$ mT, which is bound by exchange interactions (Fig. 6). In this case, the exchange between the RA of the fullerene sphere and nitroxyl is faster than in methanofullerene **1** because of the presence of two nitroxyl-containing substituents at the P atom, one of which is always close to the fullerene core. The slowness of nitroxyl-nitroxyl exchange is manifested as nonuniform broadening of some multiplet lines. The spectrum of radical anion **2** contains lines for the radical anion of mononitroxyl-containing methanofullerene owing to intramolecular reduction of nitroxyl during prolonged electrolysis.

At the potential of the second peak, the intensities of lines for the nitroxyl fragment initially increased sharply followed by their decline. At the potential of peak C_4, the signal for the nitroxyl radical disappeared; on the reverse

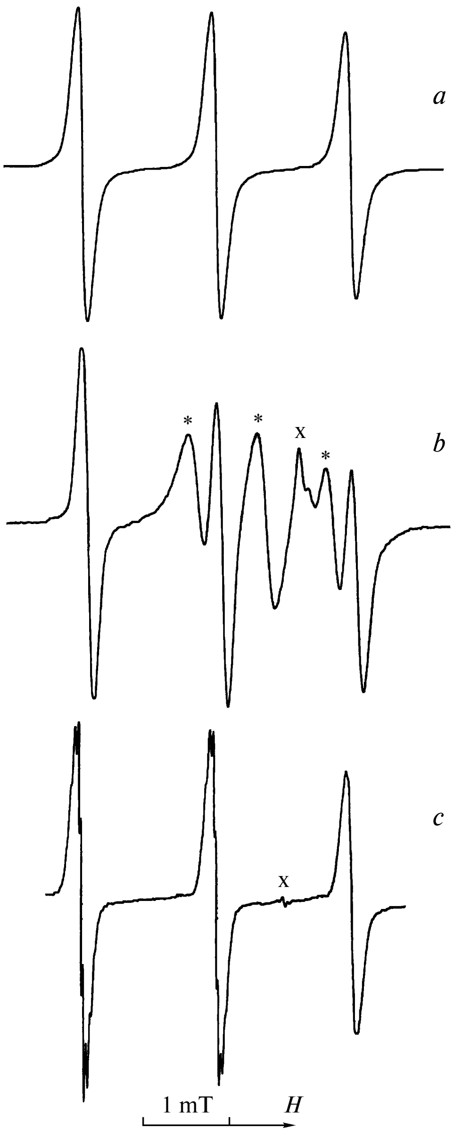


Fig. 4. ESR spectrum of a solution of methanofullerene **1** ($C = 1 \cdot 10^{-3}$ mol L^{-1}) in *o*-dichlorobenzene—DMF (3 : 1, v/v)/Bu_4NBF_4 (C = 0.1 mol L^{-1}); (*a*) the starting reagent, (*b*) upon the reduction at the potential of the first peak C_1, and (*c*) upon the reduction at the potential of the fourth step C_4 and the reoxidation at the potential A_1. The signs * and x refer to the biradical anion and fullerene-centered radical anions containing no nitroxyl fragment, respectively.

scan to the potentials of the first oxidation peak $A_1{}'$, a signal for a new nitroxyl biradical appeared (see Fig. 6). A compound of the radical nature with an analogous spectrum was isolated from products of the preparative ER at the potential of peak C_4 and reoxidation at −0.5 V (in toluene, $g = 2.0062$, $a_N = 1.54$ mT, $|J_{eff}/a_N| = 6.0$) (see Fig. 5).

In the case of compounds **1**, **2**, and **4**, the disappearance of the primary RA of methanofullerene at 313 K was accompanied by the formation of a paramagnetic product

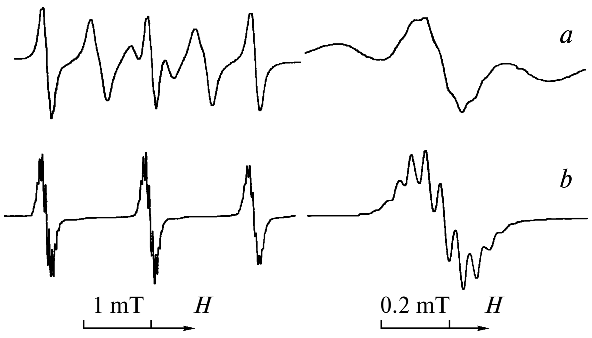


Fig. 5. ESR spectrum of a toluene solution of products obtained by preparative reduction of methanofullerenes **2** (*a*) and **1** (*b*) at the potential of the fourth step C_4 and reoxidation at the potential −0.5 V on a brass electrode with reference to Ag/0.01 *M* $AgNO_3$ in *o*-dichlorobenzene—DMF (3 : 1, v/v)/Bu_4NBF_4 (C = 0.05 mol L^{-1}).

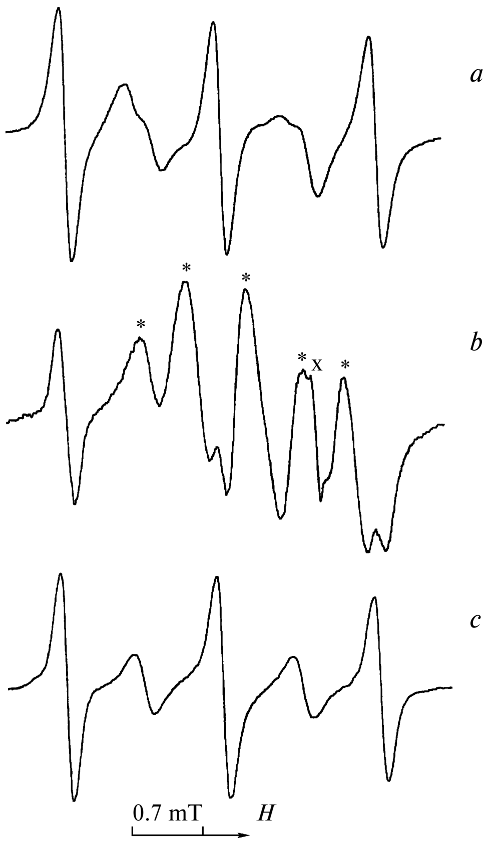
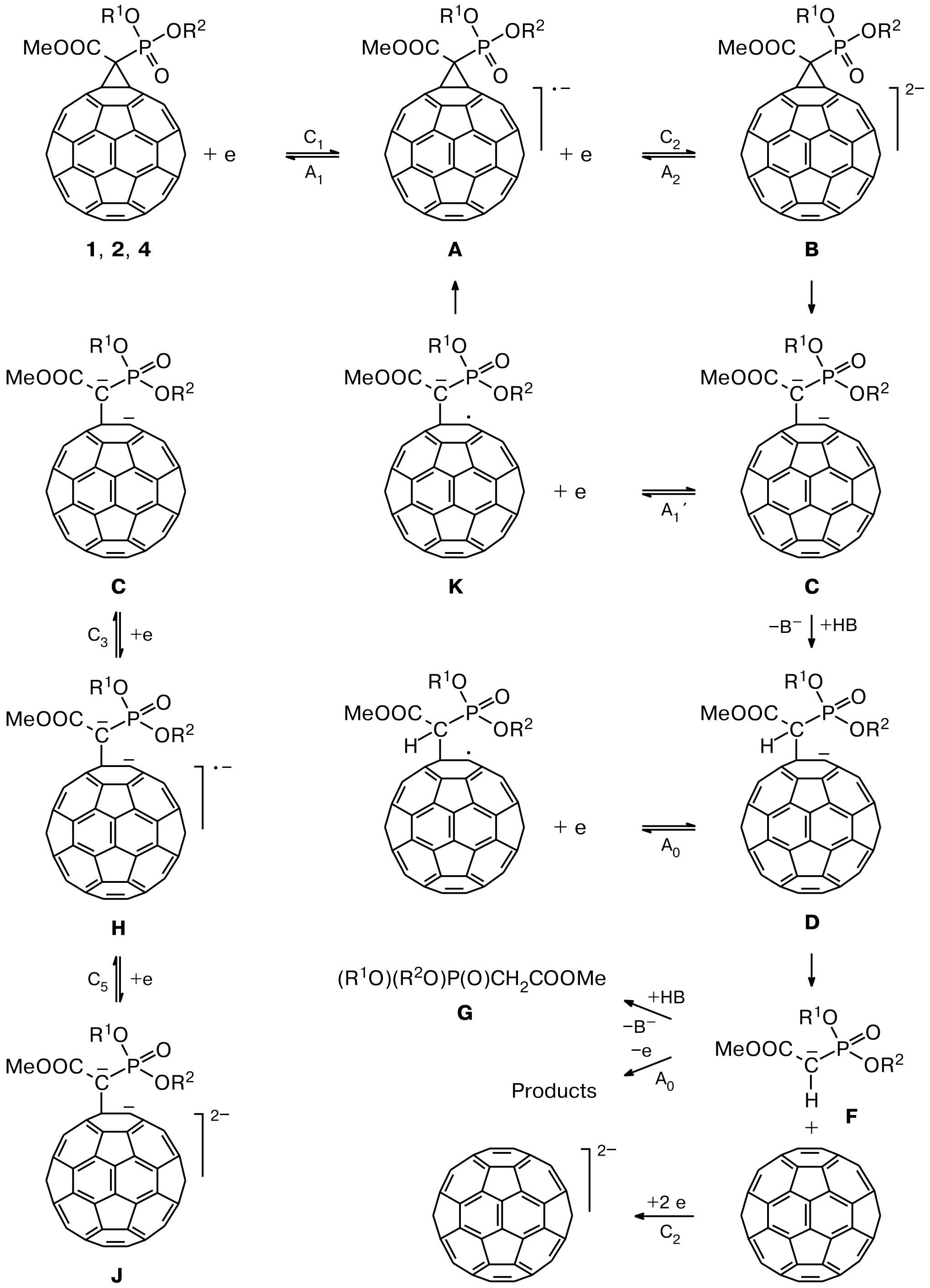


Fig. 6. ESR spectrum of a solution of methanofullerene **2** ($C = 1 \cdot 10^{-3}$ mol L^{-1}) in *o*-dichlorobenzene—DMF (3 : 1, v/v)/Bu_4NBF_4 (C = 0.1 mol L^{-1}); (*a*) the starting reagent, (*b*) upon the reduction at the potential of the first peak C_1, and (*c*) upon the reduction at the potential of the fourth step C_4 and the reoxidation at the potential A_1. The signs * and x refer to the triradical anion and fullerene-centered radical anions containing no nitroxyl radical, respectively.

with the larger *g* factor (2.0000) and the smaller line width (ΔH = 0.16 mT). The ESR parameters of this product

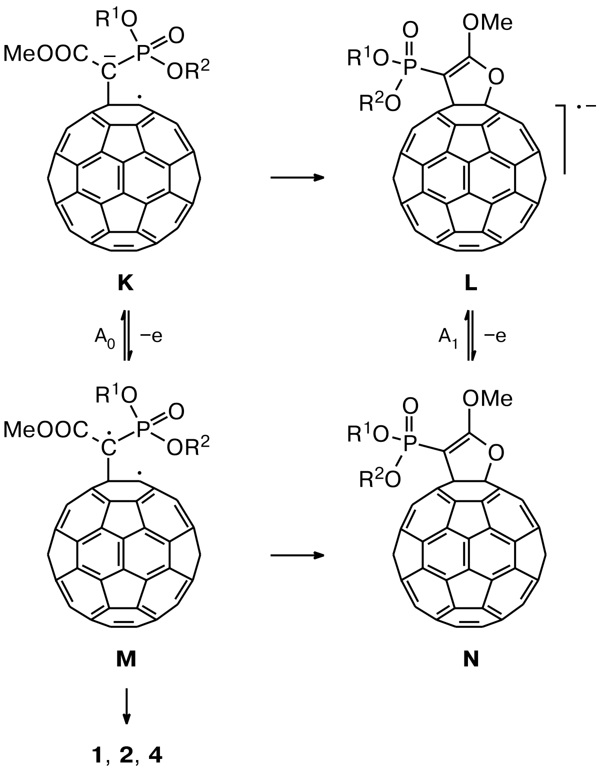
Scheme 2



correspond to the radical anions of a compound with the dihydrofuranofullerene structure.[29,30] Hence, at elevated temperature, these compounds undergo slow opening of the three-membered ring and reclosure into a five-membered dihydrofuran ring at the step of RA generation.

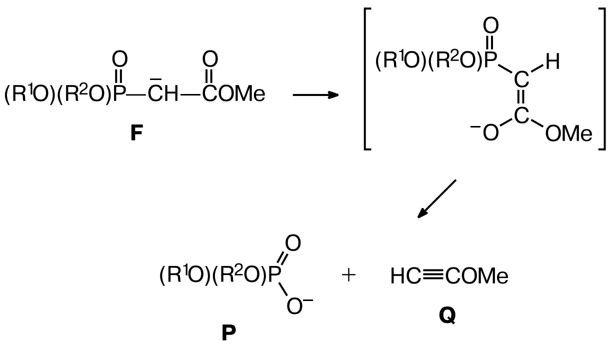
Preparative electrochemical reduction of methanofullerenes 1 and 2. Preparative ER of methanofullerene **1** (10 mg) was carried out in a divided (cellulose) cell with a cylindrical brass electrode in *o*-dichlorobenzene—DMF (3 : 1)/0.05 *M* Bu_4NBF_4 with stirring under nitrogen at room temperature. The reduction at the potential of the second peak ($E = -1.5$ V *vs.* Ag/0.01 *M* $AgNO_3$) with passing 2 F of electricity with subsequent reoxidation at $E = -0.5$ V resulted in no noticeable consumption of the starting methanofullerene **1**. According to HPLC data, the reaction mixture contained the starting compound in virtually the same concentration as before the electrolysis and only traces of free fullerene. Then, electrolysis was carried out at the potential of the fourth peak C_4 (E = −2.0 V) for 15 min (Q = 2.6 F). Reoxidation at E = −0.5 V to a constant current I = 0.3 mA (15 min) decreased 2.5-fold the concentration of methanofullerene (HPLC data). The major product was fullerene C_{60}; its content was 1.36 times higher than that of methanofullerene. In addition, a small peak eluted between methanofullerene **1** and fullerene C_{60} was detected. Earlier,[29,30] it has been demonstrated that such retention times are characteristic of dihydrofuranofullerenes obtained by ER of carbonyl-containing methanofullerenes. For this reason, we assigned this peak to dihydrofuranofullerene **1N** (Scheme 3), which was confirmed by ^{31}P NMR data.

Scheme 3



The ^{31}P NMR spectra of the reaction mixture contain two major strongly broadened signals of equal intensities at δ 2.30 and 22.32 and two minor signals at δ 11.37 and 14.82. The latter belongs to the starting methanofullerene **1**; the signal at δ 22.32 corresponds to the free monomeric hydrogenated addend **1G** (see Scheme 2), while the signals at δ 11.37 and 2.30, to fullerenodihydrofuran **1N** [29,30] and phosphate ion **1P**, respectively (Scheme 4).

Scheme 4



In the ER of methanofullerene **1** at the potential of the peak C_4 and reoxidation at the potential of the first peak, the ESR spectrum shows a line with magnetic parameters (g = 2.0000, ΔH = 0.16 mT, 313 K) corresponding to the radical anion of phosphorylated dihydrofuranofullerene.[29,30]

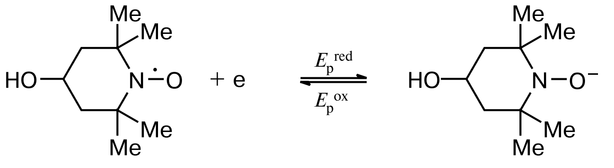
Thus, the ESR, ^{31}P NMR, and chromatographic data altogether suggest that the reduction of methanofullerene **1** at the potential of the fourth peak C_4 followed by the reoxidation at −0.5 V mainly gives free fullerene C_{60}, methyl phosphorylacetate **1G**, phosphate ion **1P**, and minor amounts of dihydrofuranofullerene **1N**.

Fullerene C_{60} is also the major product in the reduction of methanofullerene **2** at the potential of fourth peak C_4 followed by the reoxidation at E = −0.5 V (*vs.* Ag/0.01 M $AgNO_3$). As with compound **1**, chromatographic analysis also revealed dihydrofuranofullerene **2N**. Its radical anion was also detected by ESR spectroscopy (see above). In this case, much more electricity (Q = 4.4 F) was passed over the same reduction time; for this reason, the reaction mixture contained only a small amount of the starting compound, while the substantially higher concentration of free fullerene C_{60} correlated with the amount of the consumed methanofullerene **2**. According to ^{31}P NMR data, in this case, the addend was mainly eliminated as monomeric phosphonate **2G** (δ_P 23.32); phosphate ion **2P** (δ_P 2.67) formed in minor amounts.

The results obtained show that the ER of methanofullerenes **1** and **2** at the potentials of the fourth peak involves a virtually quantitative Bingel retroreaction with elimination of the addend as a carbanion stabilized by protonation yielding phosphonate **G** and by rearrangement into phosphate ion **P**. Dihydrofuranofullerene **N** forms in minor amounts.

Electrochemical behavior of nitroxyl radical 3 and methano[60]fullerene 4. The cyclic voltammogram of radical **3** contains an irreversible reduction peak at E_p^{red} = −1.95 V and a reoxidation peak at E_p^{ox} = −1.02 V (see Table 1). According to ESR data, the nitroxyl radical disappears upon the reduction but is quantitatively regenerated in the reoxidation. Hence, at these potentials, nitroxyl undergoes single-electron reduction into the hydroxylamine anion, which then reoxidizes into nitroxyl (Scheme 5).

Scheme 5



3

$E_p^{red} = -1.95$ V, $E_p^{ox} = -1.02$ V.

Note that the reduction and oxidation peaks are extended and largely differ in potentials. This indicates the slowness of electron transfer in both the forward and reverse directions, which is due to the high energy of reorganization of the molecule and of the solvation shell during electron transfer. Also note that the reduction potential is virtually equal to the potential of peak C_4 for compounds **1** and **2** and the reoxidation potential is only slightly lower than the potential of the first reoxidation peak for compounds **1** and **2**, corresponding to peak A_1'.

The CV curve of phosphorylated methanofullerene **4** contains a set of the same six reduction peaks (Fig. 7) as for compounds **1** and **2**. This methanofullerene is more difficult to reduce than both fullerene C_{60} and nitroxylmethanofullerenes **1** and **2** (see Table 1). The difference between the potentials of the first peaks of compound **4** and C_{60} in *o*-dichlorobenzene—DMF equals the respective difference in toluene—DMF (ΔE_p = 60 mV).[14,16]

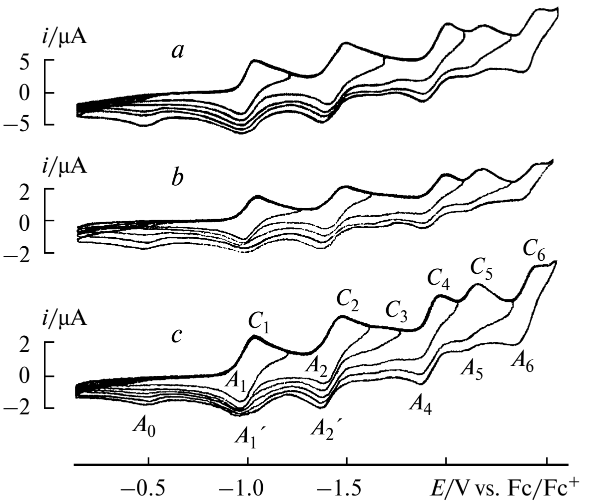


Fig. 7. Cyclic voltammograms of methanofullerene **4** ($C = 1 \cdot 10^{-3}$ mol L^{-1}) recorded with a glassy carbon electrode in *o*-dichlorobenzene—DMF (3 : 1, v/v)/Bu_4NBF_4 (C = 0.1 mol L^{-1}) at the scan rates υ = 100 (*a*), 50 (*b*), and 20 mV s^{-1} (*c*); T = 295 K.

Some facilitation of the reduction of compounds **1** and **2** as compared with methanofullerene **4** is probably due to through-space interaction of the fullerene sphere with the electron-withdrawing nitroxyl. This interaction provides an energy gain of 2.9 kJ mol^{-1} in the electron transfer.

The first reduction peaks of the fullerene sphere in methanofullerene **4** (C_1, C_2, and C_4) are equal in height and correspond to single-electron transfer. The third reduction peak C_3 is very weak and appears only at a scan rate of 20 mV s^{-1}. Peak C_5 was detected at all scan rates. The first two peaks C_1 and C_2 are reversible. The reduction at the potentials of peak C_4 results in elimination of the addend, for which reason the cathodic peak C_6 and the anodic peaks A_2', A_4, and A_6 relate to free fullerene C_{60}. In the reverse scan from the potentials of peak C_3 and the next peaks, an oxidation peak A_0 appears together with an additional anodic peak A_1' at a lower potential than that of peak A_1.

Addition of equimolar amounts of nitroxyl radical **3** to a solution of methanofullerene **4** changed only peaks C_4 and A_1' (Fig. 8*b*). Peak C_4 increased correspondingly, while peak A_1' became broader and shifted to the negative potentials, as in the case of nitroxyl-containing methanofullerenes **1** and **2**. A twofold increase in the concentration of nitroxyl **3** resulted in the increase in the heights of these peaks (see Fig. 8*a*). These results indicate that on the time scale of CV measurements (seconds), the radical anions of methanofullerene **4** are stable, while its dianions are less stable and undergo slow opening of the three-

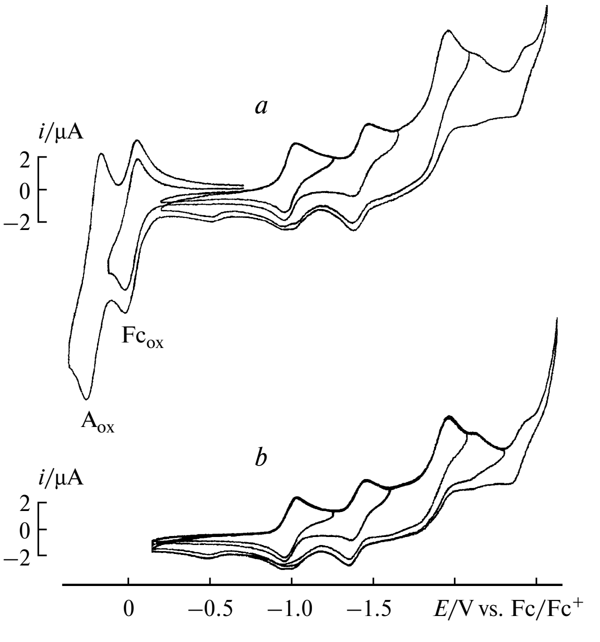


Fig. 8. Cyclic voltammograms of methanofullerene **4** ($C = 1 \cdot 10^{-3}$ mol L^{-1}) recorded with a glassy carbon electrode in *o*-dichlorobenzene—DMF (3 : 1, v/v)/Bu_4NBF_4 (C = 0.1 mol L^{-1}) at a scan rate of 20 mV s^{-1} and different concentrations of radical **3**: $2 \cdot 10^{-3}$ (*a*) and $1 \cdot 10^{-3}$ mol L^{-1} (*b*); T = 295 K.

membered ring to give an intermediate that is reduced at the potential of peak C_3. Radical anion **A** and dianion **B** (see Scheme 2) do not undergo substantial elimination of the addend nor homogeneous intermolecular reduction of nitroxyl **3**. Apparently, as with methanofullerenes **1** and **2**, neither nitroxyl nor the hydroxylamine anion react with the starting methanofullerene **4** and its reduction products. The fact that the height of the second reduction peak for compounds **1** and **2** exceeds the single-electron level is probably due to intramolecular electron transfer from the fullerene-centered dianion to the nitroxyl radical. This is evident from the lower intensity of the ESR signal for the nitroxyl radical not only for methanofullerenes **1** and **2** but also for a mixture of methanofullerene **4** with nitroxyl **3** in the reduction at the potential of the second peak. In the latter case, intermolecular electron transfer takes place. The rate of this process is significantly lower than that of intramolecular electron transfer because of the low concentrations of the compounds under study ($1 \cdot 10^{-3}$ mol L^{-1}). That is why this process can be experimentally detected only by ESR spectroscopy on sufficiently prolonged electrolysis (minutes). The result obtained suggests that, in contrast to nitroxyl-containing methano[60]fullerenes and [60]fullereno-pyrrolidines,[4–6] the fullerene sphere of compounds **1**, **2**, and **4** in *o*-dichlorobenzene—DMF/0.1 *M* Bu_4NBF_4 serves as an intra- and intermolecular electron carrier to the nitroxyl radical under the conditions of dianion generation.

Mechanism of the electrochemical reduction of methanofullerenes 1, 2, and 4. The results obtained allow us to propose a mechanism for the ER of methanofullerenes **1**, **2**, and **4**. The first step involves a reversible single-electron transfer yielding fullerene-centered RA that are stable at room temperature. At an elevated temperature, these undergo slow opening of the three-membered ring and reclosure into a five-membered ring to give a radical anion of dihydrofuranofullerene. In the case of nitroxyl-containing methanofullerenes **1** and **2**, very slow intramolecular electron transfer from the RA of the fullerene sphere to the nitroxyl radical occurs simultaneously. It takes several hours for these reactions to proceed to a noticeable extent.

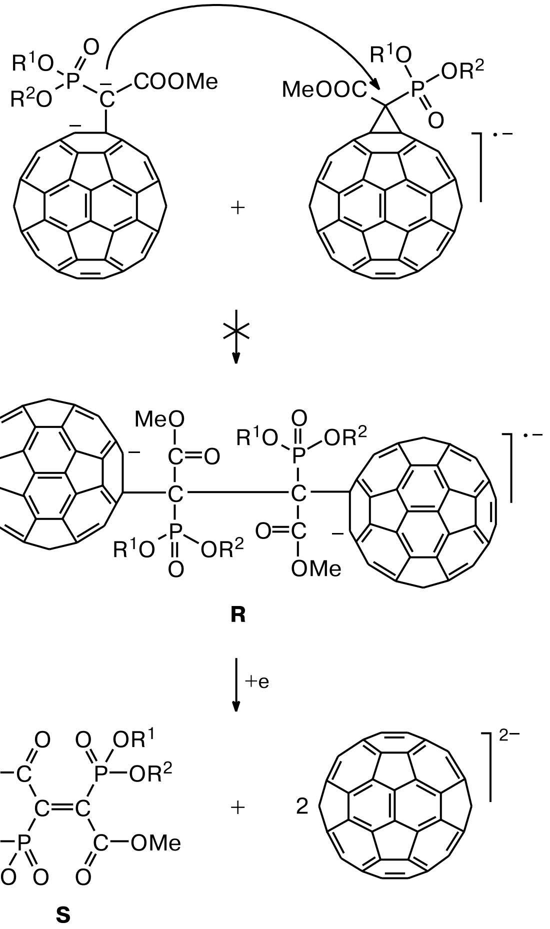
At the potential of the second reduction peak, fullerene-centered dianions (**B**) are generated. These species are unstable for all methanofullerenes and undergo opening of the three-membered ring into dianion **C** (see Scheme 2). The ring opening in dianion **B** is slow; for this reason, the cyclic voltammograms of compound **4** at all scan rates contain a virtually single-electron reduction peak of primary dianion **B** (C_4) and only a weak reduction peak of the ring opening products (C_3). Dianion **C** exhibits its weaker electron-donating and stronger electron-withdrawing properties than dianion **B** since, in contrast to the latter, one negative charge is transferred from the fullerene sphere to the addend and the other negative charge is mainly localized in position 2 of the fullerene sphere. For this reason, dianion **C** is more difficult to oxidize and less difficult to reduce than dianion **B**. Based on the aforesaid reasoning, peaks C_3 and C_5 can be attributed to the stepwise reduction of dianion **C** into radical trianion **H** and tetraanion **J**. In the case of methanofullerene **4**, peak A_1' appears at a lower potential than peak A_1. Apparently, the oxidation of dianion **C** is somewhat easier than that of the RA of methanofullerene **4**, which gives rise to an additional component that shifts peak A_1' to the more negative potentials compared to peak A_1. Radical anion **K** resulting from the oxidation of dianion **C** oxidizes at the potential of peak A_0 but it is stabilized by cyclization into the RA of the starting methanofullerene (see Scheme 2) and the RA of dihydrofuranofullerene **L** (see Scheme 3). The latter species oxidizes into a neutral compound **N** at the potential of peak A_1'. Anions **D** and **F** (see Scheme 2) oxidize at the potential of peak A_0.

Compounds **1** and **2** differ from compound **4** only in substituents in the phosphonate group. Presumably, their methanofullerene fragment undergoes the same transformations and all the relevant reasoning given above is applicable to them. Dianion **C** with the open three-membered ring and the separated negative charges on the fullerene sphere and the addend can serve as a mediator with respect to the starting methanofullerenes. In addition, this species can also act as a base or a nucleophile. Dihydrofullerene is a sufficiently strong acid (as strong as acetic acid) in the first dissociation step.[31] Therefore, the negatively charged fullerene sphere should exhibit the properties of a weak base and a weak nucleophile. Because of this, the fullerene sphere of dianion **C** in *o*-dichlorobenzene—DMF is not protonated; nor does it enter into chemical reactions. The negatively charged addend of dianion **C** is much more reactive as a base and a nucleophile. This fragment is protonated even in this medium, which results in transfer of another electron, the elimination of the addend as anion **F** (experimentally detected by ^{31}P NMR spectroscopy as phosphonate **G**), and the formation of the RA of free fullerene $C_{60}^{\bullet -}$, which is reduced at the potential of peak C_2 into dianion C_{60}^{2-} (see Scheme 2).

It was such a scheme that was considered by us in the reduction of methanofullerene **4** in toluene—DMF (2 : 1)/0.1 *M* Et_4NBF_4.[14–16] Peak A_0 was assigned to the oxidation of anion **F**. This scheme was consistent with the formation of free fullerene, the number of transferred electrons, and the absence of additional reduction peaks. The medium *o*-dichlorobenzene—DMF/0.1 *M* Bu_4NBF_4 used in the present study is probably less proton-donating and dianion **C** is insignificantly involved in such transformations on the time scale of voltammetric measurements. These reactions did not proceed quantitatively even upon prolonged preparative electrolysis (15 min), which is evident from the formation of phosphate ion **P** (see Scheme 4). Carbanions containing oxo and phosphonato groups are known[32,33] to release, under certain conditions, a phosphate ion to give the corresponding acetylene. Presumably, similar transformations are possible for anion **F** yielding electrochemically inert phosphate ion **P** and substituted acetylene **Q**.

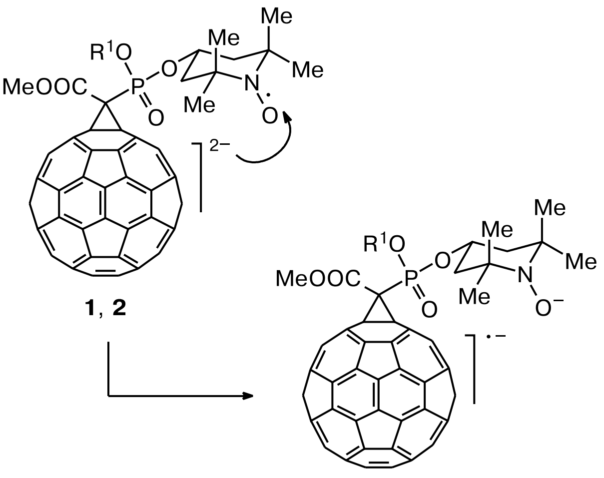
The starting methanofullerenes were synthesized by the base-catalyzed Bingel reaction of the corresponding bromo(dialkoxyphosphoryl)methoxycarbonylmethanes with fullerene C_{60}.[34] This involves a nucleophilic attack of the anions of bromo(dialkoxyphosphoryl)methoxycarbonylmethanes on fullerene. Hence, the negatively charged addends in the dianions of methanofullerenes **1**, **2**, and **4** (**C**) and other methanofullerenes that undergo opening of the three-membered ring upon the reduction can also, in principle, exhibit the nucleophilic properties with respect to the fullerene sphere and the *exo*-C(61) atom of the starting molecules and their anionic intermediates with the retained three-membered ring. The rate of such reactions will be determined by the nucleophilicity of the carbanion, the electrophilicity of the electrophile, and the steric factor. It is absolutely obvious that the nucleophilicity of the negatively charged addend singly bonded to the fullerene sphere increases with an increase in the negative charge on the fullerene sphere. At the same time, an increase in the negative charge on the fullerene sphere of the starting methanofullerenes lowers its electrophilicity and substantially facilitates the opening of the three-membered ring. All this reasoning substantiates a possible reaction of dianion **C** with the RA and/or dianion of the starting methanofullerenes to give dimeric products as shown in Scheme 6. The process follows the S_N2 mechanism with fullerene as the leaving group. Anionic dimer **R** adds an electron and releases two fullerene dianions $C_{60}{}^{2-}$ (leaving groups) to form stable unsaturated compound **S** (see Scheme 6). Generation of dimeric fullerene derivatives with bonding between the fullerene spheres upon electrochemical reduction was presumed earlier.[17,35,36] In our case, we suggest bonding between the addends in the dimers. Among the reduction products of methanofullerenes **1**, **2**, and **4**, dimeric species of neither the type **R** nor unsaturated compound **S** were detected by the methods used. These compounds are sterically overcrowded and it is for steric reasons that dimerization involving the addends seems unlikely. The probability of the formation and stability of such dimeric species increase with a decrease in the bulkiness of substituents at the C(61) atom. Therefore, the formation of sufficiently stable dimeric intermediates of this type seems to be quite probable, *e.g.*, in the reduction of the best investigated bis(alkoxycarbonyl)methanofullerenes.

Scheme 6



For compounds **1** and **2**, the aforementioned transformations in the second reduction step C_2 are accompanied by intramolecular electron transfer from dianions **B** to the nitroxyl radical (Scheme 7). This process is sufficiently fast and the degree of conversion becomes noticeable in

Scheme 7



several seconds, which was determined by cyclic voltammetry from the catalytic growth of the second peak C_2 over the single-electron level and by ESR spectroscopy from the decrease in the concentration of the nitroxyl radical. Higher reducing abilities of the dianions of fullerene derivatives as compared with their RA is quite natural; this was repeatedly demonstrated with fullerene itself as an example.[37—40] The resulting hydroxylamine anion is very stable in the medium used; it is not protonated, nor does it react with the fullerene sphere. Its reoxidation quantitatively yields the nitroxyl radical.

At the potential of peak C_4, the third electron is transferred to the fullerene sphere of the dianions of methanofullerenes **1**, **2**, and **4** with simultaneous heterogeneous and homogeneous reduction of the nitroxyl radical. The increased charge of the fullerene sphere accelerates opening of the three-membered ring into radical trianion **H** and all subsequent reactions of protonation and addend elimination, which were discussed above for dianions **C**. For this reason, the primary radical trianion is converted rapidly and quantitatively into products and thus is undetectable even by cyclic voltammetry. The resulting radical trianion **H** (see Scheme 2) is more stable and is reduced further at the potential of peak C_5, while the radical trianion of free fullerene is reduced at the potential of peak C_6. The dianions of the starting methanofullerenes and fullerene C_{60} oxidize at the potential of peak A_2'. The fullerene dianions are more difficult (by 30—60 mV) to oxidize than the methanofullerene dianions, that is why the overall peak A_2' appears at a higher potential than peak A_2. At the potential of peak A_1', the primary RA of methanofullerenes **1**, **2**, and **4**, the RA of free fullerene, the hydroxylamine anion, and dianion **C** oxidize. All these species are reduced at slightly different potentials and their near-electrode concentrations are different, for which reason the peak is broadened and shifted to the more negative potentials. Peak A_0 is attributed to the oxidation of anions **D**, **F**, and **K**.

The suggested reduction scheme describes the processes altogether occurring in the electrochemical reduction of methanofullerenes **1**, **2**, and **4** over a wide potential range and allows the experimentally observed reduction and oxidation steps to be correlated with the transformations of these compounds and their anionic intermediates. Obviously, real processes are even more complex. In particular, not only the processes considered above but also other homogeneous processes of intermolecular electron transfer from more charged intermediates to less charged ones become evident from the potentials of the corresponding reduction peaks and the stabilities of fullerene-centered anionic intermediates. We discussed such processes in more detail with other methanofullerenes and fullerenopyrrolidines as examples. However, these reactions probably do not change the pathways of the transformations or the nature of the resulting products.

Experimental

Fullerene C_{60} from the G. A. Razuvaev Institute of Organometallic Chemistry (Russian Academy of Sciences) was of 99.9% purity. Organic solvents were dried and distilled.

Cyclic voltammograms were recorded on a PI-50-1 potentiostat connected to an H 307/2 XY-recorder. A glassy carbon disk electrode (d = 2 mm) press-fitted into a fluoroplastic holder served as a working electrode. The electrode was mechanically polished each time before measurements. Potentials were measured with respect to a standard potential of the ferrocene/ferrocenium ion (Fc/Fc^+) redox system versus Ag/0.01 M $AgNO_3$ in MeCN as a reference electrode. Dissolved oxygen was removed by bubbling nitrogen through solutions at 295 K.

ESR study together with *in situ* electrolysis was carried out at 313 K on a setup combining a SE/X-2544 ESR spectrometer, a PI-50-1 potentiostat, and an electrochemical cell. The setup allows an electrochemical process to be carried out in the resonator of the ESR spectrometer. A platinum coil served as a working electrode, a platinum wire, as an auxiliary electrode, and a silver wire, as the reference electrode. Solutions were deaerated by three sequential freezing—evacuation—thawing cycles.

UV spectra were recorded on a Specord M-40 spectrophotometer in THF—$CHCl_3$ (10 : 2). IR spectra were recorded on a Bruker-Vector 22 Fourier spectrometer (pellets with KBr). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker MSL 400 and Bruker Advance 600 spectrometers (100.57 (^{13}C), 162.00 (^{31}P), and 400.00 and 600.00 MHz (^1H)) in $CDCl_3$ with Me_4Si and 85% H_3PO_4 as standards. Mass spectra of methyl [methoxy(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yloxy)phosphoryl]acetate and methyl bis(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yloxy)phosphorylacetate were recorded on a Finnigan MAT-212 instrument (ionizing energy 60 eV, electron emission current 0.1 mA, m/z 200—1500, direct inlet probe, evaporator temperature ~300 °C). The mass spectra of methanofullerenes **1** and **2** were recorded on a MALDI-TOF DYNAMO TERMOBIOANALYSIS mass-spectrometer (Germany).

Preparative electrochemical reduction was carried out with a PI-50-1 potentiostat in a divided (cellulose) glass cell on a cylindrical brass electrode (S = 16.4 cm^2) at a controlled potential in o-dichlorobenzene—DMF (3 : 1, v/v)/0.05 M Bu_4NBF_4 under nitrogen at 295 K. The anodic compartment was placed in a brass cylinder filled with a supporting electrolyte. A platinum coil was used as an anode and Ag/0.01 M $AgNO_3$ in MeCN was used as the reference electrode.

61-[Methoxy(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yloxy)phosphoryl]-61-methoxycarbonylmethano[60]fullerene (1). Methyl [methoxy(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yloxy)phosphoryl]acetate (**5**) was prepared according to a known procedure[10] and isolated as an individual compound by column chromatography on SiO_2. Its composition was confirmed by mass spectra showing a molecular ion peak with m/z 322. ^{31}P NMR ($CDCl_3$), δ: 22.44.

1,8-Diazabicyclo[5.4.0]undec-7-ene (0.137 g, 0.9 mmol) was added in an argon atmosphere to a mixture of C_{60} (0.216 g, 0.3 mmol), CBr_4 (0.149 g, 0.45 mmol), and phosphorylacetate **5** (0.145 g, 0.45 mmol) in anhydrous toluene (200 mL). The reaction mixture was kept at 40 °C for 12 h. The precipitate was filtered off and the filtrate was washed with water (3×30 mL) and concentrated. Column chromatography on SiO_2 recovered fullerene C_{60} (0.056 g) (elution with toluene—hexane (1 : 3)); compound **1** (0.054 g, 23% with respect to the consumed fullerene) was eluted with toluene—acetonitrile (1 : 19), m.p. >350 °C. MS (MALDI TOF), m/z ($I_{\rm rel}$ (%)): 1042.275 (34), 1024.605 (20); 887.883 (22); 856.604 (20). Calculated: 1040.994. UV (CH_2Cl_2), $\lambda_{\max}$/nm: 257, 326, 427.8, 492.7, 707. IR (KBr), ν/cm^{-1}: 526, 578, 669, 710, 753, 800, 927, 1009, 1046, 1180, 1233, 1269, 1362, 1429, 1460, 1640, 1739, 2853, 2926; ^{31}P NMR ($CDCl_3$), δ: 15.03. ^{13}C NMR ($CDCl_3$), δ: 68.58, 69.02 (sp^3-hybridized C atoms); 135.72, 135.79, 139.68, 139.76, 139.82, 139.90, 139.96, 140.64, 140.94, 140.98, 141.57, 141.86, 141.95, 141.98, 142.67, 142.70, 142.85, 142.94, 143.27, 143.49, 143.61, 143.69, 143.85, 144.03, 144.15, 144.24, 146.06, 163.38 (sp^2-hybridized C atoms of the fullerene cage); 186.57 (C=O).

61-Methoxycarbonyl-61-bis(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yloxy)phosphorylmethano[60]fullerene (2). Methyl bis(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yloxy)phosphorylacetate (**6**) was prepared according to a known procedure[11] and isolated as an individual compound by column chromatography on SiO_2. Its composition was confirmed by mass spectra showing a molecular ion peak with m/z 462.6. ^{31}P NMR ($CDCl_3$), δ: 25.05.

1,8-Diazabicyclo[5.4.0]undec-7-ene (0.137 g, 0.9 mmol) was added in an argon atmosphere at room temperature to a stirred mixture of C_{60} (0.216 g, 0.3 mmol), CBr_4 (0.149 g, 0.45 mmol), and phosphorylacetate **6** (0.208 g, 0.45 mmol) in anhydrous toluene (200 mL). The reaction mixture was stirred at 35 °C for 5 h, the precipitate was filtered off, and the filtrate was washed with water (3×30 mL) and concentrated. Column chromatography on SiO_2 recovered fullerene C_{60} (0.053 g) (elution with toluene—hexane (1 : 3)); compound **2** (0.043 g, 16%) was eluted with toluene—acetonitrile (37 : 3), m.p. >350 °C.

MS (MALDI TOF), m/z ($I_{\rm rel}$ (%)): 872.736 (40.3), 1028.969 (39.0); 1182.850 (41.1). Calculated: 1181.201. UV (CH_2Cl_2), $\lambda_{\max}$/nm: 258, 326, 427.9, 492, 707. IR (KBr), ν/cm^{-1}: 527, 579, 671, 711, 755, 801, 833, 880, 928, 994, 1046, 1180, 1238, 1271,1362, 1430, 1463, 1635, 1740, 2861, 2930, 2971. ^{31}P NMR ($CDCl_3$), δ: 17.23. ^{13}C NMR ($CDCl_3$), δ: 53.67, 69.23, 69.64 (sp^3-hybridized C atoms); 136.16, 136.24, 140.18, 140.23, 140.32, 141.06, 141.39, 141.42, 141.47, 142.02, 142.30, 142.41, 142.44, 143.12, 143.15, 143.27, 143.59, 143.71, 143.93,143.97, 144.06, 144.12, 144.17, 144.24, 144.46, 144.58, 144.65, 146.66, 163.69 (sp^2-hybridized C atoms of the fullerene cage); 193.23 (C=O).

Electrochemical reduction of methano[60]fullerene 1. A working solution (15 mL) was prepared by dissolving methanofullerene **1** (10 mg, 9.6 μmol) in *o*-dichlorobenzene—DMF (3 : 1, v/v)/0.05 *M* Bu_4NBF_4 with stirring. HPLC analysis of the reaction mixture was performed on a Gilson chromatograph equipped with a UV detector (λ = 325 nm) and a column with the reversed phase C-18 (Partisil 5-ODS-3); toluene—acetonitrile (2 : 3, v/v) was used as an eluent. For the reaction mixture: ^{31}P NMR, δ: 22.32, 14.83, 11.38, 2.30.

Electrochemical reduction of methanofullerene 2. A working solution (15 mL) was prepared by dissolving methanofullerene **2** (10 mg, 8.5 μmol) in *o*-dichlorobenzene—DMF (3 : 1, v/v)/0.05 *M* Bu_4NBF_4. Electrolysis and chromatographic analysis of the reaction mixture were carried out as described for compound **1**. For the reaction mixture: ^{31}P NMR, δ: 23.22, 2.67.

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