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ESR parameters and transformations of the products of reduction of methanofullerenes

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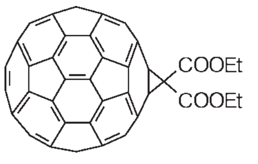
Paramagnetic products of chemical (by diazabicycloene derivatives) and electrochemical reduction of the dicarbethoxy derivative and phosphorylated methane[60]fullerenes were studied by ESR. In all cases, one-electron reduction affords radical anions ($g = 1.9998—1.9999$, $\Delta H = 0.20—0.28$ mT), and further reduction produces the secondary radicals ($g = 2.0004—2.0010$, $\Delta H = 0.020—0.028$ mT). The rate constants for formation and decay of the radical anions in chemical reduction depend slightly on the nature of the reducing agent and substituents in the methanofullerenes. The retro-Bingel reaction occurs during two-electron reduction.

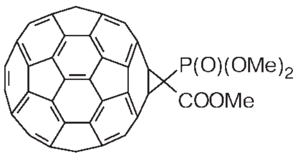
Key words: fullerene C_{60}, methanofullerenes, organophosphorus compounds, electroreduction, ESR spectroscopy, radical anions.

It is known[1—4] that the reduction of fullerene C_{60} affords stable anionic intermediates. The first stage of this process, resulting in radical anions (RA), can easily occur through electron transfer from various reducing agents. We have earlier studied the mechanism of electrochemical reduction (ER) of various, including phosphorylated, methanofullerenes.[5,6] We showed that the RA that formed are stable for several seconds, and during electrolysis at potentials of the second and third electron transfer to the methanofullerene molecule the bonds of the fullerene sp^3-hybridized C atoms with the exocyclic C atom are cleaved to form fullerene C_{60}. However, in the case of *N*-methylfulleropyrrolidines the ER does not result in the cleavage of the bonds between the sp^3-hybridized C atoms of the fullerene shell and the C atoms of the pyrrolidine cycle.[7] Distinctions in the electrochemical behavior of fullerene C_{60} derivatives provide new possibilities for fullerene functionalization, especially in the syntheses of compounds containing substituents in a specified position of the fullerene molecule.

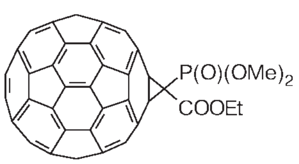
In this connection, it seems of interest to study the products formed by electron transfer to the functionally substituted fullerene molecule from various electron donors. In this work, we studied the reduction of the dicarbethoxy derivative (**1a**) and phosphorylated methane[60]fullerenes (**1b—d**) both under electrolysis conditions and in reactions with organic electron donors, *viz.*, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).



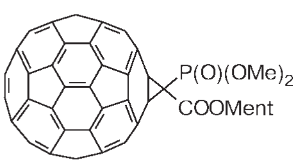
1a



1b



1c



1d

Ment is menthyl

Experimental

Synthesis and properties of methanofullerenes **1b—d** were described earlier.[8] Fullerene derivative **1a** was synthesized using a known procedure.[9]

Electroreduction of compounds **1a—d** was studied by ESR combined with electrolysis in the toluene—DMF (1 : 1 v/v) system against the background of 0.1 *M* Et_4NBF_4. The concentration of methanofullerenes **1a—d** was $1 \cdot 10^{-3}$ mol L^{-1}. Solvents were purified using standard procedures. ER experiments were carried out at 298 K on a setup combining an SE/X-2544 ESR spectrometer, a PI-50-1 potentiostat, and an electrochemical cell, which allowed electrolysis in the resonator of the ESR spectrometer. A Pt coil served as the working electrode, a Pt

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wire was the auxiliary electrode, and an Ag wire served as the reference electrode. Solutions were deaerated using three freezing—evacuation—thawing out cycles.

Compounds **1a—d** were chemically reduced by DBU and DBN in a sealed glass ampule at 298 K in the resonator of the ESR spectrometer.

Preparative ER of methanofullerene **1a** followed by oxidation was carried out in a cell with a cellulose diaphragm in the potentiostatic regime in a toluene—DMF (1 : 1 v/v) medium with 0.1 *M* Et_4NBF_4 as the supporting electrolyte using a PI-50-1 potentiostat. A Pt wire with a surface area of 0.5 cm^2 served as the working electrode, and a Pt network was the anode. During electrolysis the solution was stirred by an Ar flow at 20 °C. Electrolysis was conducted at the potential $E = -1.5$ V *vs.* Ag/0.01 *M* $AgNO_3$ and then at −0.6 V until the initial current decreased by 90%.

The working solution (5 mL) was prepared by the dissolution of compound **1a** (4.2 mg, $5 \cdot 10^{-6}$ mol) and Et_4NBF_4 (0.12 g, 0.5 mmol) in the toluene—DMF solvent. After the end of electrolysis, the solution was analyzed by HPLC using a Gilson chromatograph with a UV detector (column with the reverse C_{18} phase (Partisil-5 ODS-3), eluent toluene—MeCN (1 : 1 v/v)). Besides the initial compound **1a**, only fullerene C_{60} was isolated in 61% yield.

Results and Discussion

The products generated by one-electron transfer at the potentials of the first reduction stage and those formed by the reaction of an organic electron donor with the fullerene derivative molecule have virtually the same magnetic parameters. The ESR spectra exhibit one line, whose magnetic parameters and limiting intensity are independent of the method of preparation of the paramagnetic species (Table 1, Fig. 1).

The one-electron ER of methanofullerenes **1a—d** affords RA. Therefore, RA of methanofullerenes are precisely the species which are detected in chemical reduction (Scheme 1).

Table 1. Characteristics of the RA of methanofullerenes **1a—d** generated through electrochemical reduction and by the reaction with DBN in the toluene—DMF (1 : 1 v/v) system

Compound	*g* Factor	Δ*H*/mT	$k_1{}^a \cdot 10^4$	$k_2{}^b \cdot 10^{55}$
			s^{-1}	
1a	1.9998	0.28	4.3	8.4
1b	1.9999	0.21	2.6	3.3
1c	1.9999	0.21	3.1	3.3
1d	1.9999	0.20	2.8	2.7

[a] Rate constant for RA formation at the initial moment of reduction with 20-fold excess DBN.

[b] Rate constant for RA decay after their maximum concentration was achieved during reduction with 20-fold excess DBN.

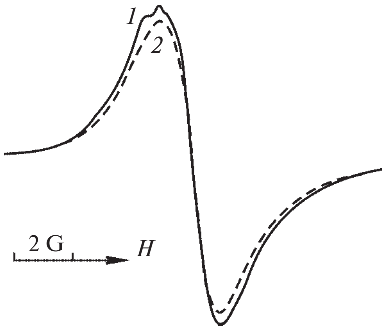
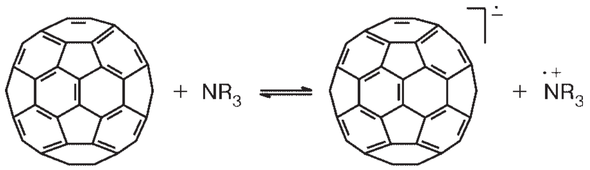


Fig. 1. ESR spectrum of the radical anion and secondary radical species generated by the reaction with DBU (*1*) and electrochemical reduction (*2*) of a solution of **1d** ($1 \cdot 10^{-3}$ mol L^{-1}) in the toluene—DMF (1 : 1 v/v) medium.

Scheme 1



$$\overset{\cdot +}{NR_3} + \text{Solv} \longrightarrow H^+ + \text{Prod}$$

$$NR_3 + H^+ \longrightarrow H\overset{+}{N}R_3,$$

Solv is solvent, Prod are products, NR_3 is DBN or DBU

The potentials of the reduction of methanofullerenes and oxidation of amines differ widely ($\Delta E_p > 1.2$ V), and electron transfer between these molecules is possible only when the transformations of amine radical cations are rapid and irreversible. In fact, we failed to detect the amine radical cations by ESR. We did not study the further transformations of the radical cations of amines. However, it is evident that any reaction pathway produces protons, whose number should correspond to the number of transferred electrons. Protons, in turn, are bound by excess amine to form ammonium ions. The experimental detection of the RA of the fullerene derivative ($Ful^{\cdot -}$) upon reduction with amines implies that $Ful^{\cdot -}$ is protonated by the ammonium ions to an insignificant extent if any.

The absence of HFS with the P nucleus in the β-position to the fullerene shell in the ESR spectra of $Ful^{\cdot -}$ attracts attention. Perhaps, this is associated with an insignificant contribution of the sp^3-hybridized C atoms of the fullerene shell to the delocalization of the excess electron density. These data agree with the results of works,[10,11] which show that the spin density in the RA of fulleropyrrolidines is mainly localized at the C atoms in the equatorial region of the fullerene shell. Some line narrowing in the ESR spectra of compounds **1a—d** is a result, to a greater extent, of the asymmetry of the fullerene shell changing in the series **1a** > **1b** ≈ **1c** > **1d** rather than the electronic properties of the substituents at the *exo*-C atom. A possible decrease in the symmetry of molecules **1a—c** is confirmed, in our opinion, by an increase in the number of signals from the sp^2-hybridized C atoms of the fullerene shell in the ^{13}C NMR spectra.[8] Therefore, the linewidth in the ESR spectrum is due to the violation of the J_h-symmetry of the initial fullerene rather than the interaction of the unresolved HFS with magnetic nuclei.

The lines of the RA of **1a—d** are not saturated when the microwave power increases. The linewidth decreases with an increase in the degree of asymmetry of the molecule, most likely, due to dynamic processes of the conformational or vibrational character, which occur in the ESR time scale and broaden the lines in the ESR spectra of the methanofullerene RA (dynamic Jahn—Teller effect).

The intensity of the ESR signal of the RA formed by both ER and reduction with amines first increases and then slowly decreases (Fig. 2), which indicates the subsequent RA transformations. The DBU and DBN reactants manifest approximately the same reductive properties. The rate constants for the formation (k_1) and decay (k_2) of Ful$^{\bullet -}$ during chemical reduction are somewhat higher for dicarbethoxymethanofullerene **1a** and almost the same for phosphorylated methanofullerenes **1b—d** (see Table 1). This result seems quite reasonable because it has been shown previously[5,6] that the rate constants of elimination of the methane fragment in the methanofullerene dianions slightly depend on the nature of substituents at the *exo*-C atom.

The transformations of the RA are rather slow: no noticeable signal from the secondary products is observed during voltammetric measurements (seconds).[5,6] However, during plolong electrolysis or the reduction of the fullerene derivatives with DBU and DBN new radical species appear, along with the RA, with the *g* factors in the 2.0004—2.0010 region and lifetime ~10—100 min. These species, as a rule, exhibit the linewidth by an order of magnitude shorter than that characteristic of the RA (see Fig. 2). The formation of such species was found in several works.[12,13] The characteristic property of these secondary radicals is the achievement of the limiting equilibrium concentrations regardless of the method of reduction of compounds **1a—d**.

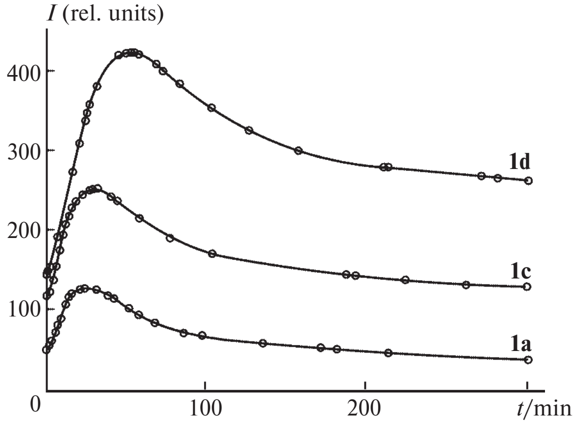


Fig. 2. Temporal change in the intensity of lines from the radical anions of **1a**,**c**,**d** during reduction with 20-fold excess DBN.

The most likely pathway of decay of organic RA involves their protonation. Only unsubstituted fullerene C$_{60}$ was isolated upon the preparative ER of compounds **1a** at the strictly monitored potential of the second peak (E = -1.5 V) followed by oxidation at -0.6 V. In the case of the fullerene derivatives with very low reduction potentials the decay of the comparatively stable RA seems to occur only to an insignificant extent. These reactions, probably, are very significant for chemical reduction by amines because, in this case, the medium becomes proton-donating during the reaction. For ER secondary radical species are, most probably, dimeric derivatives of fullerenes **1a—d** formed by the reversible dimerization or disproportionation of the anionic intermediates. These species are in mobile chemical equilibrium with the primary RA and dianions (Scheme 2). Perhaps, these radicals also undergo other transformations, including those accompanied by the elimination of the methane fragment through the retro-Bingel reaction.[5,6,13]

Scheme 2

$$\mathrm{Ful}^{2-} + \mathrm{Ful} \rightleftharpoons 2\,\mathrm{Ful}^{\bullet -}$$

$$\mathrm{Ful}^{\bullet -} + \mathrm{Ful} \rightleftharpoons \mathrm{Ful}^{-}\text{—}\mathrm{Ful}^{\bullet}$$

$$\mathrm{Ful}^{2-} + \mathrm{Ful} \rightleftharpoons \mathrm{Ful}^{-}\text{—}\mathrm{Ful}^{-}$$

Electroreduction at the potentials of the second peak, *i.e.*, under the conditions of Ful^{2-} dianion generation, does not produce new lines in the ERS spectrum but is accompanied by a decrease in the intensity of the signals from the RA (**1a—d**) and an increase in the signals from the secondary radical species.

When the potential is switched off, the intensity of the ESR lines of radical anions **1**$^{\bullet -}$ increases due to electron transfer between the dianions and initial methanofullerenes

$$\mathrm{Ful}^{2-} + \mathrm{Ful} \rightleftharpoons 2\,\mathrm{Ful}^{\bullet -}.$$

This also indicates that the Ful^{2-} dianions are diamagnetic or the ESR lines are low-intensity because of a great linewidth or a low content of paramagnetic species.

In addition, a broad line (ΔH ~7 mT) of the RA of unsubstituted fullerene C_{60} appears in the ESR spectra after some time, which confirms our conclusion for the preparative electrolysis of **1a** and the previous conclusion[5,6] based on voltammetric measurements that the methano fragment is eliminated from the Ful^{2-} dianions.

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