

Electrochemical reduction of some methanofullerenes. On the mechanism of the retro-Bingel reaction

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The reactions of electrochemical reduction of methanofullerenes bearing phosphonate and alkoxy carbonyl groups at the *exo*-carbon atom were studied. The mechanism of the retro-Bingel reaction as the cleavage of two C—C bonds between the C(61) atom and the fullerene shell accompanied by electrochemical electron transfer was proposed.

Key words: phosphonomethanofullerene, electrochemical reduction, Bingel reaction, retro-Bingel reaction.

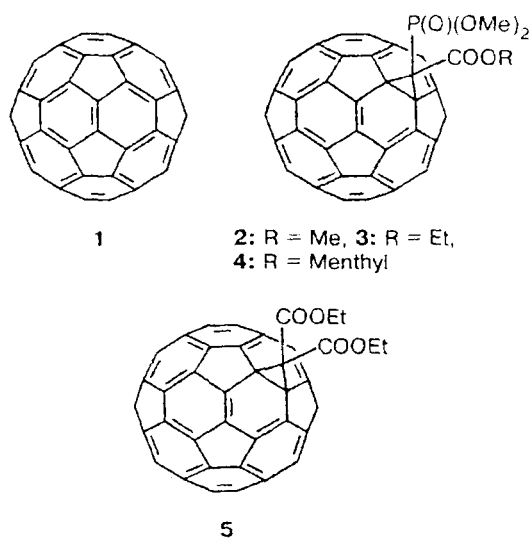
Recently, considerable attention has been focused on the methods of preparation of new functionally substituted derivatives of fullerenes^{1,2} due to a search for novel materials and biologically active compounds.^{3,4} In this connection methanofullerenes containing functionally substituted cyclopropane fragments condensed with the fullerene ring at the 6,6-bond^{5,6} assume a great significance.

Different approaches to the synthesis of compounds of this type are known: addition of carbenes, nucleophilic addition of carbanions of halogen-containing compounds followed by the elimination of a halide anion and cyclization to methanofullerenes.^{7,8} Bingel was the first to describe the nucleophilic cycloaddition—elimination in the fullerene series to form methanofullerenes.⁹ More recently, this reaction has widely been used for syntheses of various derivatives of methanofullerenes, including preparation of biologically active compounds.^{10,11} We have described the synthesis of phosphorylated methanofullerenes by the general pattern of the Bingel reaction from fullerene C₆₀ (1) and alkoxyphosphoryl bromoacetates.¹²

It has been shown in several works that the ability to accept readily electrons in both the electrochemical reactions¹³ and the interaction with organic electron donors¹⁴ is a characteristic property of fullerene and its derivatives.

In this work, we used the cyclic voltammetry (CV) method to study the electrochemical reduction of phosphorylated methanofullerenes (2–4) and dicarboethoxymethanofullerene (5) synthesized by us, and their behavior was compared to that of fullerene C₆₀ (1).

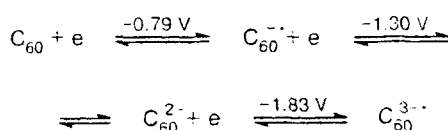
Three reduction peaks and, correspondingly, three oxidation peaks are observed (Fig. 1) on the CV curves of C₆₀ and methanofullerenes 2–5 obtained on the Pt electrode in a toluene—DMF (2 : 1) solution against



0.1 M Et₄NBF₄. The characteristics of the peaks are presented in Table I.

The successive transfer of three electrons is observed for C₆₀ (Scheme 1).

Scheme 1



Reduction of compounds 2–5 occurs virtually at the same potentials, but it is somewhat more difficult than

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 426–429, March, 2000.

that of C_{60} . The characteristics of the reversible transfer of the first electron coincide for compounds 2–5. The potentials of the second peak of these compounds are constant; however, the number of electrons consumed in this step (n) ranges from 1.19 to 1.25. Some difference of the number of transferred electrons (2.72 to 2.82) and in the reduction potentials (–1.85 to –1.87 V) is observed in the third step. The fractional value of n per molecule of methanofullerenes 2–5 at the potentials of the second and third peaks has engaged our attention, whereas the total value of n in these steps is

always equal to four. The n value depends on the potential sweep V . As V decreases, n increases at potentials of the second peak and decreases at potentials of the third peak. However, the total number of electrons transferred in these steps remains to be four (Table 2).

The data obtained indicate the reduction of compounds 2–5 at potentials of the second and third steps via the mechanism with the switched-on chemical stage

Table 1. Parameters of peaks of reduction of fullerene C_{60} (1) and compounds 2–5 on the Pt electrode in a toluene–DMF (2 : 1, v/v) mixture against Et_4NBF_4 ^a

Compound	E_p^{red}/V^b	n^c	E_p^{ox}/V^b	$\Delta E_p/mV^d$	k_1/s^{-1}
C_{60} (1)	–0.79	1.00	–0.73	60	
	–1.30	1.00	–1.23	70	
	–1.83	1.00	–1.76	70	
	–0.85	1.00	–0.79	60	
2	–1.34	1.24	–1.27	70	0.32
	–1.85	2.72	–1.75	100	
	–0.85	1.00	–0.79	60	
	–1.34	1.19	–1.27	70	
3	–1.86	2.81	–1.75	110	0.29
	–0.85	1.00	0.79	60	
	–1.34	1.19	–1.27	70	
	–1.87	2.82	–1.75	120	
4	–0.85	1.00	0.79	60	0.24
	–1.34	1.19	–1.27	70	
	–1.87	2.82	–1.75	120	
	–0.85	1.00	0.79	60	
5	–1.34	1.25	–1.28	60	0.31
	–1.85	2.79	–1.75	100	
	–0.85	1.00	0.79	60	
	–1.34	1.19	–1.27	70	

^a Conditions: $C_1 = 1 \cdot 10^{-3}$ mol L^{–1}, 25 °C, $V = 100$ mV s^{–1}.

^b The potentials were measured versus Ag/0.01 M AgNO₃ in MeCN (E_p^{red} are the reduction potentials, and E_p^{ox} are the oxidation potentials of the reduction products obtained by the CV method).

^c The number of electrons determined by comparison with the one-electron peaks of C_{60} .

^d The difference of potentials between the cathodic and anodic peaks.

Table 2. Number of electrons (n) transferred per molecule of compounds 2–5 at potentials of the first (n_1), second (n_2), and third (n_3) reduction peaks

Compound	$V/mV s^{-1}$	n_1	n_2	n_3	$n_2 + n_3$
2	20	1.00	1.41	2.59	4.00
	50	1.00	1.33	2.67	4.00
	100	1.00	1.24	2.72	3.96
	200	1.00	1.18	2.82	4.00
3	20	1.00	1.32	2.68	4.00
	50	1.00	1.34	2.66	4.00
	100	1.00	1.19	2.81	4.00
	200	1.00	1.19	2.81	4.00
4	20	1.00	1.24	2.76	4.00
	50	1.00	1.22	2.73	3.95
	100	1.00	1.19	2.82	4.01
	200	1.00	1.17	2.83	4.00
5	20	1.00	1.32	2.68	4.00
	50	1.00	1.29	2.76	4.05
	100	1.00	1.25	2.79	4.04
	200	1.00	1.19	2.74	4.03

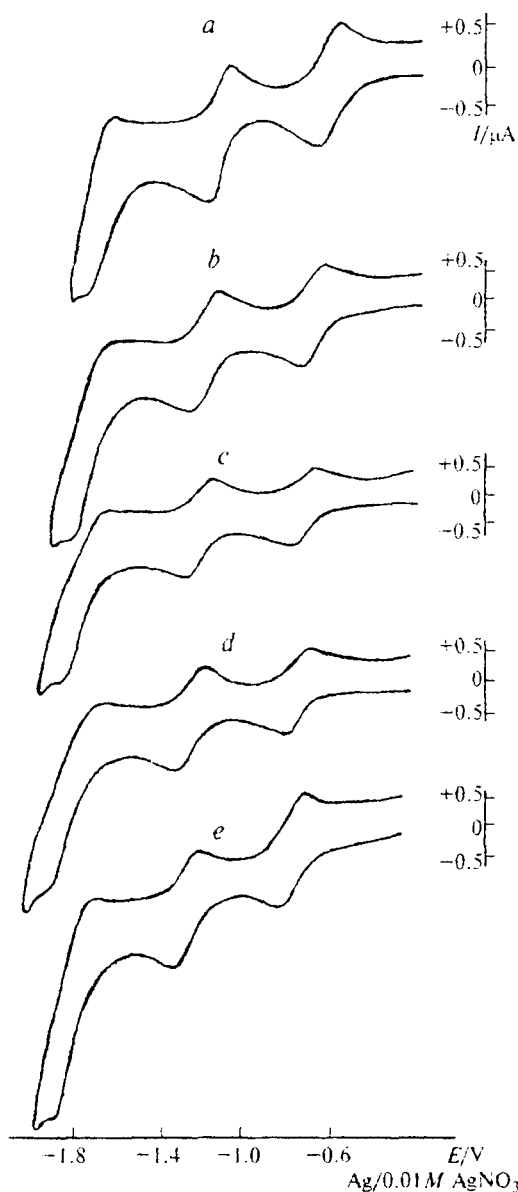
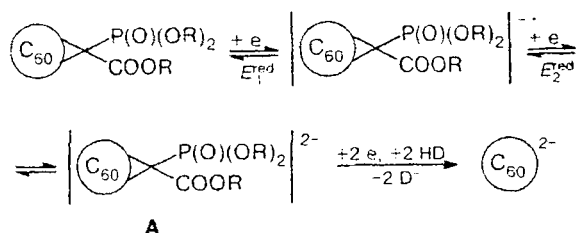


Fig. 1. Cyclic voltammograms of fullerene C_{60} (a) and compounds 2 (b), 3 (c), 4 (d), and 5 (e) on the Pt electrode in the toluene–DMF (2 : 1)/0.1 M Et_4NBF_4 mixture; $V = 100$ mV s^{–1}, 25 °C, $C_1 = 5 \cdot 10^{-4}$, $C_{2-5} = 1 \cdot 10^{-3}$ mol L^{–1}.

(ECE process). At potentials of the second peak, the chemical stage is slow, *i.e.*, its rate is lower than the rate of diffusion of molecules 2–5 to the electrode surface, whereas it is fast at potentials of the third peak (the rate of the chemical stage is higher than the diffusion rate of molecules of the substance to the electrode surface). The oxidation potential of the products of reduction of compounds 2–5 at potentials of the third peak ($E_p^{ox} = -1.75$ V) virtually coincides with the oxidation potential of the radical trianion of fullerene C_{60} , which implies fast elimination of substituents from the radical trianions of compounds 2–5. The radical trianion of C_{60} and the corresponding esters of phosphonoacetic or malonic acids or their carbanions are formed due to these transformations. It is known from the literature¹⁵ that the reduction of compound 5 at potentials of the second peak and subsequent oxidation of the reduction products result in fullerene C_{60} . The authors¹⁵ did not explain the mechanism of the observed reaction, although they named this electrochemical transformation as the "retro-Bingel reaction." It is most likely that a slow step-by-step cleavage of two C–C bonds of the fullerene shell with the bridging fragment and elimination of the corresponding esters to form the C_{60}^{2-} dianion (Scheme 2) occur in dianions of compounds 2–5 in a toluene–DMF system and in CH_2Cl_2 .

Scheme 2

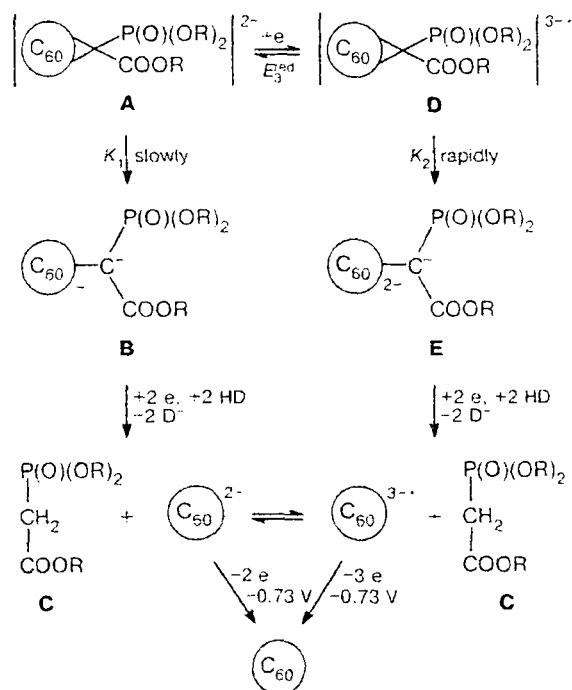


Using the empirical Nicholson correlation¹⁶ for ECE processes, we estimated the rate constant k_1 of this stage (Table 1). As can be seen in Table 1, the rate constants of cleavage of two carbon–fullerene bonds are approximately equal for compounds 2–5. In our opinion, this is an additional proof that the transition from di-(alkoxycarbonyl)methanofullerene 5 to alkoxycarbonyl(alkoxyphosphoryl)methanofullerenes 2–4 does not substantially change the character of binding of the methane fragment to the fullerene shell.

To obtain fullerene C_{60} in the retro-Bingel reaction under study, it is necessary that the reduction process generating the C_{60}^{2-} dianion be followed by oxidation of the latter occurring at a potential of -0.73 V. The aforesaid is valid for the electrochemical transformations at potentials of the third peak rather than the second peak.

The reduction of compounds 2–5 at potentials of three waves can be described by the following scheme (Scheme 3).

Scheme 3

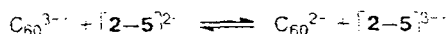


Dianion A, whose formation is shown in Scheme 2, undergoes a slow transformation into dianion B with one cleaved carbon–fullerene ring bond. This dianion B, being reduced in the presence of proton donors, is transformed into the C_{60}^{2-} dianion, which at a potential of -0.73 V donates two electrons and is transformed into free C_{60} and phosphonoacetate C.

At the same time, dianion C_{60}^{2-} can be reduced to form radical trianion C_{60}^{3-} , which at a potential of -0.73 V, donating three electrons, can give free C_{60} . As mentioned above, at the step of the third reduction peak, the contribution of chemical transformations is much more pronounced than that at the step of the second reduction peak. Radical trianion D formed at this step is rapidly transformed into the trianion with the open three-membered cycle E, which, withdrawing two electrons in the presence of a proton donor, is transformed into the radical trianion C_{60}^{3-} . The routes of transformation of this radical trianion into free C_{60} are shown above.

We do not discuss other routes of formation of the retro-Bingel reaction products, but believe that it is significant that our data indicate the possibility of both heterogeneous (on the electrode) and homogeneous (in

the solution) reactions of methanofullerene reduction. Under homogeneous conditions, the radical trianion of fullerene C_{60}^{3-} , which is formed in the electrochemical reduction of methanofullerenes at potentials of the third wave, can serve as a reducing agent. All conditions necessary for this process are fulfilled: a high stability of the radical trianion of fullerene C_{60} , a low difference of potentials of the transfer of the third electron to molecules of C_{60} and methanofullerenes **2–5**, and a high rate of the irreversible cleavage of the methanocarbon–fullerene bond in radical trianions of compounds **2–5**. Although we did not verify experimentally the occurrence of homogeneous electron transfer processes, based on a high electron affinity of fullerene C_{60} and its derivatives, we assume the parallel occurrence of heterogeneous (on the electrode) and homogeneous (by radical trianions of C_{60}) reactions of electrochemical reduction of methanofullerenes at potentials of the third wave.



Probably, a similar scheme is valid for the electrochemical reduction of other methanofullerenes. Note that electrochemical reduction of organic compounds is usually characterized by C–C bond formation processes (homo- and cross-coupling).¹⁷ Cleavage of C–C bonds in reduction is a sufficiently rare phenomenon.¹⁸ It is most likely that the driving force of the observed cleavage of two C–C bonds in the methanofullerene reduction is the tendency to "aromatization" of the fullerene fragment, which is facilitated by two pronounced withdrawing groups at methano carbon and thermodynamic stability of the carbanion formed. This can somewhat be confirmed by a slight increase in the reduction potential when electron-withdrawing groups are added to fullerene C_{60} .

Experimental

Electrochemical reduction of fullerene C_{60} and compounds **2–5** was studied by cyclic voltammetry in a toluene–DMF (2 : 1) system against 0.1 M Et_4NBF_4 . Cyclic voltammograms were recorded on a PI-50-1 potentiostat and a PDP-4 two-coordinate recorder using a Pt electrode sealed into the glass. The reference electrode was Ag/0.01 M $AgNO_3$ in MeCN, and a platinum wire served as an auxiliary electrode. The concentration of the depolarizer was $1 \cdot 10^{-3}$ mol L⁻¹ (fullerene C_{60} , $5 \cdot 10^{-4}$ M). Working solutions were deaerated with nitrogen, and the temperature was 25 °C. Fullerene C_{60} used had 99.9%

purity (according to the HPLC data). The synthesis of compounds **2–4** was described in Ref. 12, and compound **5** was prepared by the known procedure.⁹ Solvents were purified by standard procedures.

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

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Received September 6, 1999