

# Electrochemical behavior and parameters of hydrofullerene C<sub>60</sub>H<sub>36</sub>

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Electrochemistry of hydrofullerene C<sub>60</sub>H<sub>36</sub> was studied by cyclic voltammetry in THF and CH<sub>2</sub>Cl<sub>2</sub> in the -47–14 °C temperature range. Hydrofullerene undergoes reversible one-electron reduction to form a radical anion in THF ( $E^0 = -3.18$  V (Fc<sup>0</sup>/Fc<sup>+</sup>), Fc = ferrocene) and irreversible one-electron oxidation in CH<sub>2</sub>Cl<sub>2</sub> ( $E_p^a = 1.22$  V (Fc<sup>0</sup>/Fc<sup>+</sup>)). The reduction potential was used to estimate electron affinity of hydrofullerene as EA = -0.33 eV. It was suggested that C<sub>60</sub>H<sub>36</sub> is an isomer with *T*-symmetry in which 12 double bonds form four isolated benzenoid rings located in vertices of an imaginary inscribed tetrahedron on the molecular surface. For hydrofullerene, the "electrochemical gap" is an analog of the energy gap (HOMO–LUMO), equal to ( $E^{ox} - E^{red}$ ) = 4.4 V, and indicates that C<sub>60</sub>H<sub>36</sub> is a sufficiently "hard" molecule with a low reactivity in redox reactions.

**Key words:** hydrofullerene, C<sub>60</sub>H<sub>36</sub>, redox properties, cyclic voltammetry, electron affinity, electrochemical gap.

Presently, C<sub>60</sub>H<sub>2</sub> and C<sub>70</sub>H<sub>2</sub> are the only electrochemically characterized<sup>1</sup> hydrofullerenes. It is established<sup>2,3</sup> that, similarly to fullerenes, the reduction of hydrofullerenes includes several one-electron, mainly reversible, steps, but with potentials 100–180 mV more negative than those for the corresponding fullerenes. In addition, C<sub>60</sub>H<sub>2</sub> undergoes irreversible two-electron oxidation accompanied by the ejection of two protons followed by regeneration of C<sub>60</sub>.<sup>1,2</sup> Hydrofullerenes with a higher content of hydrogen were not electrochemically characterized. Perhaps, this is related to their very low solubility in most solvents appropriate for electrochemical studies.

Electrochemistry and reactivity of both hydrofullerenes and their radical ion states are of doubtless interest. In addition to information on the reactivity of electrogenerated radical ions, these data provide valuable information on boundary orbitals (HOMO, LUMO, etc.). The problem of the structure of hydrofullerene C<sub>60</sub>H<sub>36</sub> remains unclear up to now.<sup>4,5</sup> The theoretical calculations predict that hydrofullerene C<sub>60</sub>H<sub>36</sub> has 10<sup>13</sup> isomers.<sup>6</sup> The four most stable isomers of hydrofullerene C<sub>60</sub>H<sub>36</sub> with *T*-, *T<sub>h</sub>*-, *D<sub>3d</sub>*-, and *D<sub>3d</sub>*'-symmetry are considered in the literature. They differ in arrangement of 12 double bonds on the molecular surface which remain after hydrogenation of C<sub>60</sub> (Fig. 1). In the isomer with *T*-symmetry, 12 double bonds form four isolated benzene rings located in vertices of an imaginary inscribed tetrahedron on the molecular surface. In the isomer with *T<sub>h</sub>*-symmetry, 12 isolated double bonds are arranged in five-membered rings, whereas in the isomers with *D<sub>3d</sub>*- and *D<sub>3d</sub>*'-symmetry, six double bonds are located on poles of the molecule as benzene rings,

and the other six double bonds are parallel to the equator of the molecule (*D<sub>3d</sub>*) or are arranged at an angle to the equator (*D<sub>3d</sub>*'). Our studies of C<sub>60</sub>H<sub>36</sub> by <sup>13</sup>C and <sup>1</sup>H NMR,<sup>4,5</sup> X-ray photoelectron, and emission spectroscopy<sup>7,8</sup> showed that the hydrofullerene is, most probably, an isomer with *T*-symmetry. Electrochemical study of hydrofullerene can provide additional data on the assumed isomeric structures.

In this work, we present the results of a cyclic voltammetric study of the electrochemical behavior of hydrofullerene C<sub>60</sub>H<sub>36</sub> in THF and CH<sub>2</sub>Cl<sub>2</sub> in a wide temperature range (-47–14 °C). The experimental reduction and oxidation potentials of hydrofullerene were used for calculation of its electrochemical parameters.

## Results and Discussion

Due to low solubility in THF, the reduction of C<sub>60</sub>H<sub>36</sub> was studied on a glassy-carbon electrode with a rather large surface (0.07 cm<sup>2</sup>). In the studied temperature interval (-47–14 °C) at potential sweeps (v) of 20–200 mV s<sup>-1</sup>, the cyclic voltammograms (CV) of C<sub>60</sub>H<sub>36</sub> at *E* < -2 V exhibit four diffusionally controlled ( $I_p \cdot v^{-1/2} = \text{const}$ , where *I<sub>p</sub>* is the height of the peak) cathodic peaks (A, B, C, and D) with different heights and reversibilities (Fig. 2, curve 1). The potentials of these peaks *E<sub>p</sub><sup>c</sup>* or formal redox potentials ( $E^0 = (E_p^c + E_p^a)/2$ , where *E<sub>p</sub><sup>c</sup>* and *E<sub>p</sub><sup>a</sup>* are the potentials of the cathodic and anodic peaks, respectively) for the corresponding redox pairs are presented in Table 1. Since hydrofullerene is poorly soluble in both pure THF and its mixtures with toluene,<sup>5</sup> measurements were car-

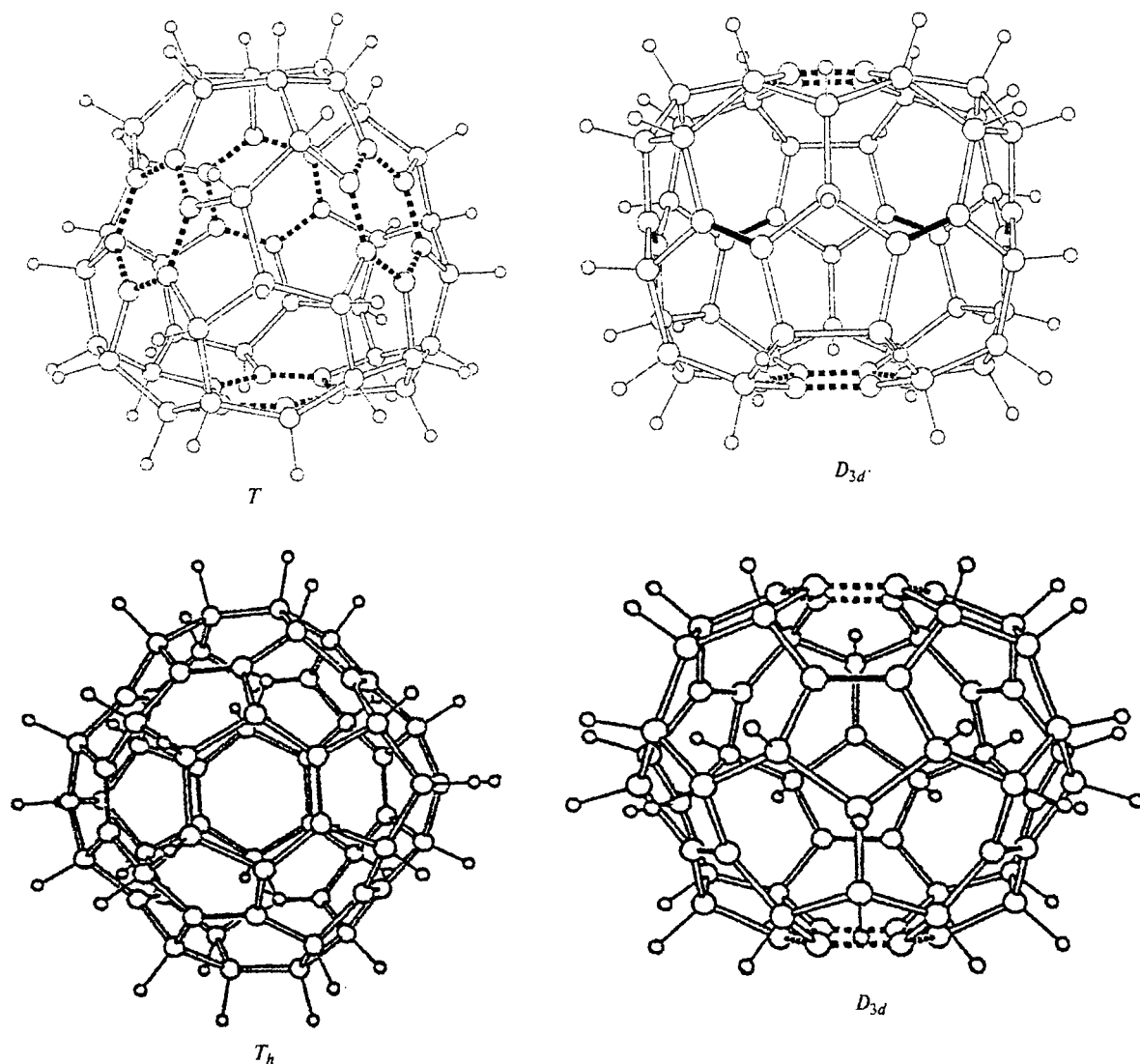


Fig. 1. Structures of isomers of hydrofullerene  $C_{60}H_{36}$  calculated by the semiempirical PM3 method.<sup>8</sup> Formally double bonds are designated by solid lines, and benzene fragments are shown by dotted lines.

ried out in saturated solutions of  $C_{60}H_{36}$  (with concentrations of  $\sim 1 \cdot 10^{-5}$  mol  $L^{-1}$ ).

According to the procedure of preparation of  $C_{60}H_{36}$  from  $C_{60}$  by the hydrogenation of the latter with 9,10-dihydroanthracene,<sup>5</sup> even after purification of target hydrofullerene by vacuum sublimation, it contains trace (to 0.5–1.0 wt.%) amounts of anthracene,<sup>9,10</sup> whose solubility is much higher than that of  $C_{60}H_{36}$ . It is clear that when a saturated solution of  $C_{60}H_{36}$  is prepared, anthracene (1) goes from the sample to the solution. Therefore, the reversible pair of peaks A/A' is attributed to the redox pair  $1^0/1^-$ , which is confirmed by CV of the authentic sample 1 (Table 1). In addition, peak C is also referred to the reduction of 1 ( $1^- \xrightarrow{-e} 1^{2-}$ ) (see Table 1, Fig. 2, curve 3, and Ref. 11). Thus, the reduction of hydrofullerene  $C_{60}H_{36}$

is characterized by the reversible pair of peaks D/D'. The nature of the irreversible peak B, which is poorly pronounced on the CV, is yet unclear.

Despite the problems concerning the low solubility of  $C_{60}H_{36}$ , it is evident that the quasi-reversible cathodic peak D is one-electron. This follows from  $\Delta E_p = E_p^a - E_p^c \approx 140$  mV for this peak at  $-38^\circ C$ . Note for comparison that for the certainly reversible  $Fc^0/Fc^+$  redox pair,  $\Delta E_p$  is  $\sim 80$  mV at room temperature.

Oxidation of  $C_{60}H_{36}$  was studied in  $CH_2Cl_2$  at  $-47^\circ C$  on a glassy-carbon electrode. The CV of hydrofullerene contains three diffusionally controlled ( $I_p \cdot v^{-1/2} = \text{const}$ , where  $I_p$  is the height of the peak) irreversible anodic peaks (E, F, and G, Fig. 3, curve 1), whose potentials ( $E_p^a$ ) are presented in Table 1. It can be seen in Fig. 3 that anodic peaks E and G on the

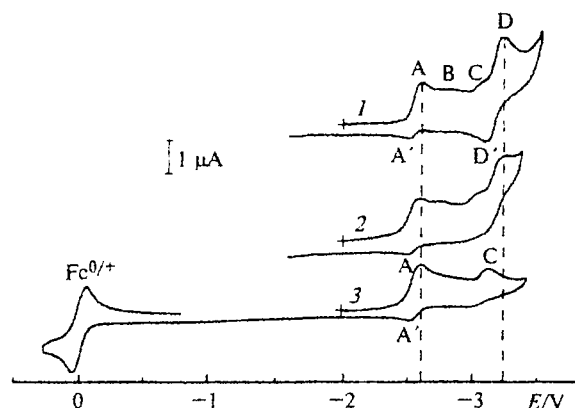


Fig. 2. Cyclic voltammograms of saturated solutions of hydrofullerene  $C_{60}H_{36}$  (1, 2) and anthracene (3;  $5 \cdot 10^{-4}$  mol  $L^{-1}$ ) on a glassy-carbon electrode ( $v = 0.2$  V  $s^{-1}$ ) in THF/0.05 M  $Bu_4NPF_6$  at -38 (1) and 14 °C (2, 3).

CV of hydrofullerene are attributed to anthracene (cf. curves 1 and 2). Peak E should be assigned to the reversible redox pair  $I^0/I^{+}$  (peaks E/E', Fig. 3, curve 3), and peak G corresponds to the irreversible redox transition  $I^{+}/I^{2+}$ , which is confirmed by the CV of the authentic sample 1 (Table 1). The electrogenerated radical cation  $I^{+}$  probably reacts with  $C_{60}H_{36}$ , resulting in irreversibility of peak E on the CV of hydrofullerene. Thus, the oxidation of hydrofullerene  $C_{60}H_{36}$  characterizes the irreversible peak F ( $E_p^a = +1.22$  V ( $Fc^0/Fc^+$ )). It is noteworthy that the oxidation of  $C_{60}H_{36}$  occurs at more positive potentials than that of  $C_{60}H_2$  ( $E_p^a = +1.13$  V ( $Fc^0/Fc^+$ ) in benzonitrile<sup>2</sup>), but at more negative potentials than that of  $C_{60}$  ( $E_p^a = +1.39$  V ( $Fc^0/Fc^+$ ) in  $CH_2Cl_2$  at 25 °C (see Ref. 12)).

Table 1. Potentials of peaks on cyclic voltammograms of hydrofullerene  $C_{60}H_{36}$  and anthracene on a glassy-carbon electrode ( $v = 0.2$  V  $s^{-1}$ ) relative to the  $Fc^0/Fc^+$  redox pair

Compound	Solvent	$T/^{\circ}C$	Peak	$E^0(E_p)^*/V$
$C_{60}H_{36}$	THF	+14	A/A'	-2.56
			B	(-2.77)
			C	(-3.13)
			D	(-3.24)
	THF	-38	A/A'	-2.56
			B	(-2.84)
			C	(-3.13)
			D/D'	-3.18
	$CH_2Cl_2$	-47	E	(0.88)
			F	(1.22)
Anthracene	THF	+14	A/A'	-2.57
			C	(-3.13)
	$CH_2Cl_2$	-47	E/E'	0.85
			G	(1.57)

\* The potentials of irreversible peaks are shown in parentheses.

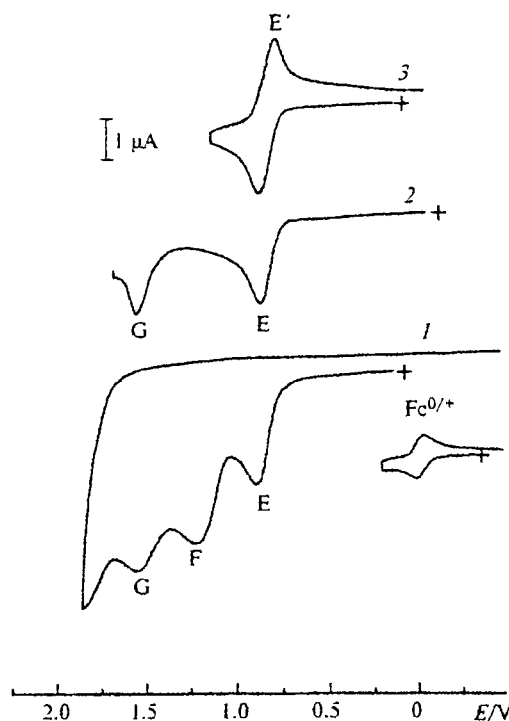


Fig. 3. Cyclic voltammograms of saturated solutions of hydrofullerene  $C_{60}H_{36}$  (1) and anthracene (2, 3;  $5 \cdot 10^{-4}$  mol  $L^{-1}$ ) on a glassy-carbon electrode ( $v = 0.2$  V  $s^{-1}$ ) in  $CH_2Cl_2$ /0.05 M  $Bu_4NPF_6$  at -47 °C.

The reversible reduction ( $E^0 = -3.18$  V, ( $Fc^0/Fc^+$ )) and irreversible oxidation ( $E_p^a = +1.22$  V ( $Fc^0/Fc^+$ )) peaks observed on the CV of hydrofullerene  $C_{60}H_{36}$  should be attributed to an isomer with  $T$ -symmetry rather than to those with  $T_h$ -,  $D_{3d}$ -, or  $D_{3d}'$ -symmetry. This assumption is based on the fact that compounds containing benzene rings are reduced at more negative potentials (for example, for benzene,  $E^0 = -3.81$  V ( $Fc^0/Fc^+$ ) in THF<sup>13</sup>) than those containing double bonds (see Ref. 14).

Using the reduction potential of hydrofullerene, we can estimate its electron affinity (EA) by the following equation:

$$E^0 = EA - \Delta\Delta G + \text{const}, \quad (1)$$

where  $E^0$  and EA are the experimentally measured reduction potential of the molecule in the liquid phase and its electron affinity in the gas phase, respectively, and  $\Delta\Delta G$  is the difference in energies of solvation of neutral molecules and their anions, which depends on the nature of the solvent and supporting electrolyte. The constant in Eq. (1) depends on the reference electrode used.

It can be assumed that under similar experimental conditions (a solvent/supporting electrolyte and a reference electrode),  $\Delta\Delta G$  for hydrofullerene  $C_{60}H_{36}$  with

**Table 2.** Electrochemical parameters of fullerene C<sub>60</sub>, hydrofullerenes, and benzene

Compound	$E^{\text{Ox}}/\text{V}$	$E^{\text{Red}}/\text{V}$	$\chi/\text{V}$	$G/\text{V}$	References
C <sub>60</sub>	1.39	-1.04	0.17	2.43	1
C <sub>60</sub> H <sub>2</sub>	1.13	-1.04	0.05	2.17	2
C <sub>60</sub> H <sub>36</sub>	1.22	-3.18	-0.98	4.40	*
C <sub>6</sub> H <sub>6</sub>	1.86	-3.82	-0.98	5.67	13

\* This work.

*T*-symmetry and benzene would be approximately the same, because good correlations by Eq. (1) are known<sup>15</sup> for fullerenes, their derivatives, and aromatic compounds. The calculation of the electron affinity of hydrofullerene by Eq. (1) gives EA = -0.33 eV (cf. the corresponding values for benzene,  $E^0 = -3.81$  V (Fc<sup>0</sup>/Fc<sup>+</sup>); EA = -1 eV). The negative electron affinity of hydrofullerene is also confirmed by quantum-chemical calculations using the semiempirical PM3 method (EA = -0.51 eV),<sup>8</sup> non-empirical calculations in the approximation of the local density functional (EA = -0.24 ± 0.03 eV),<sup>16</sup> as well as by studies<sup>17,18</sup> of hydrofullerene C<sub>60</sub>H<sub>36</sub> by mass spectrometry of negative ions, which showed the presence of the peak of the negative ion C<sub>60</sub>H<sub>18</sub><sup>-</sup> and the absence of the peaks of the negative ion C<sub>60</sub>H<sub>36</sub><sup>-</sup> in the spectra. This experimental fact indicates that C<sub>60</sub>H<sub>36</sub> has a negative electron affinity, whereas C<sub>60</sub>H<sub>18</sub> possesses a positive electron affinity.

The reactivity of hydrofullerene C<sub>60</sub>H<sub>36</sub> in redox reactions can be predicted by the "inherent electrochemical gap" (*G*) and electrochemical electronegativity ( $\chi$ ), which can be calculated from the experimental reversible reduction and oxidation potentials of the molecules:  $G = E^{\text{Ox}} - E^{\text{Red}}$  and  $\chi = (E^{\text{Ox}} + E^{\text{Red}})/2$  (see Ref. 19). The *G* and  $\chi$  values for fullerene C<sub>60</sub>, hydrofullerenes C<sub>60</sub>H<sub>2</sub> and C<sub>60</sub>H<sub>36</sub>, and benzene are presented in Table 2.

The oxidation potentials for hydrofullerenes are irreversible; therefore, strictly speaking, they cannot be used to calculate, for example, reactions of these compounds, but such calculations give good results for the comparative estimation of these values.<sup>19,20</sup> It can be seen in Table 2 that *G*, which is an analog of the energy gap (HOMO—LUMO), is ~2 times higher for C<sub>60</sub>H<sub>36</sub> than those for C<sub>60</sub> and hydrofullerene C<sub>60</sub>H<sub>2</sub> and approaches the value for benzene. Based on this, we can assume that C<sub>60</sub>H<sub>36</sub> manifests itself as a rather "hard" molecule with a low reactivity in redox reactions. The electrochemical electronegativity decreases in the series C<sub>60</sub> > C<sub>60</sub>H<sub>2</sub> > C<sub>60</sub>H<sub>36</sub> ≈ C<sub>6</sub>H<sub>6</sub> and is negative and almost equal for the two latter compounds. This indicates the close nature of these compounds and additionally favors *T*-symmetry of hydrofullerene C<sub>60</sub>H<sub>36</sub>.

### Experimental

Hydrofullerene C<sub>60</sub>H<sub>36</sub> was prepared by hydrogenation of C<sub>60</sub> (through hydrogen transfer from 9,10-dihydroanthracene

to fullerene) and purified according to the previously described procedure.<sup>5</sup> The samples of hydrofullerene thus obtained contained 0.5–1 wt.% admixtures of anthracene according to the data of spectrophotometric analysis. Hydrofullerene is poorly dissolved in solvents used for electrochemical studies, and its concentration in solutions was ~10<sup>-5</sup> and ~10<sup>-4</sup> mol L<sup>-1</sup> in THF and CH<sub>2</sub>Cl<sub>2</sub>, respectively. Thus, when C<sub>60</sub>H<sub>36</sub> samples are incompletely dissolved, the concentrations of hydrofullerene and anthracene in solutions are comparable.

Voltammetric measurements were carried out in an atmosphere of dry argon in solvents pre-purified and distilled directly into an evacuated and filled with argon electrochemical cell according to the previously described procedure.<sup>21</sup> THF (Aldrich) was purified by the "ketyl" method, and CH<sub>2</sub>Cl<sub>2</sub> (Aldrich) was purified by refluxing above P<sub>2</sub>O<sub>5</sub>. An 0.05 *M* solution of Bu<sub>4</sub>NPF<sub>6</sub> was used as the supporting electrolyte. Tetrabutylammonium hexafluorophosphate (Aldrich) was pre-dehydrated by melting in a vacuum. Low-temperature electrochemical measurements were carried out during thermostating of the cell with a mixture of ethanol with liquid nitrogen in a Dewar flask.

All measured potentials are presented relative to the redox pair Fc<sup>0</sup>/Fc<sup>+</sup> by referring the potential of the reference electrode (an Ag/AgCl/4 *M* aqueous solution of LiCl), which was separated from the solution under study in the cell with a bridge filled with a solution of the supporting electrolyte, to that of the redox transition Fc<sup>0</sup>/Fc<sup>+</sup> ( $E^0 = 0.44$  V, SCE in THF and 0.43 V in CH<sub>2</sub>Cl<sub>2</sub>). All voltammograms were first recorded in the absence of Fc, which was added in the end of each experiment.

A glassy-carbon disk electrode (3 mm in diameter, Tokai, Japan) sealed into glass and polished by a diamond paste (grain size ≤ 1 mm) was used as a working electrode. Voltammetric measurements were carried out on a PAR 175 signal-generator and a PAR 173 potentiostat with compensation of ohmic losses. Voltammograms were recorded on an RE0074 two-coordinate recorder.

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