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Relationship between reduction potentials and electron affinities of fullerenes and their derivatives

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A linear relationship was found between the first reduction potentials (E°_{red}) and electron affinities (*EA*) for fullerenes C_{60} and C_{70}, their hydro- and fluoro-derivatives, and aromatic hydrocarbons: $E^\circ_{red} = -3.04 + 0.81 \cdot EA$. This equation was used to estimate the unknown values of EA = 2.45 eV for $C_{60}H_2$, 2.47 eV for $C_{70}H_2$, −0.15 eV for $C_{70}H_{36-38}$, −0.41 eV for $C_{70}H_{44-46}$, and $E^\circ_{red} = -1.74$—-1.91 V (*vs.* $Fc^{0/+}$) for $C_{60}H_{18}$.

Key words: fullerenes, hydrofullerenes, fluorofullerenes, aromatic hydrocarbons, redox potentials, electron affinity, linear relationship.

The discovery of fullerenes and synthesis of functional derivatives of these compounds stimulated their comprehensive research,[1] in particular, electrochemical study.[2] The first reduction potentials (E°_{red}) in the liquid phase, which are reversible most often, and gas phase electron affinity (*EA*)[3,4] are especially important parameters of these compounds. These two magnitudes should linearly be related between each other by the equation[3]

$$E^\circ_{red} = EA + \text{const}, \qquad (1)$$

where const = $-\Delta\Delta G_{sol} + E_{ref}$ ($\Delta\Delta G_{sol}$ is the difference in solvation energies of neutral molecules and their anions, which depends on the nature of the solvent and supporting electrolyte, and E_{ref} is the constant related to the potential of the reference electrode). These linear relationships were established[5,6] for the following series: fullerenes C_{60}—C_{86}, fluorofullerene $C_{60}F_{48}$, and fullerenes C_{60}—C_{92}. Equation (1) allows one to predict E°_{red} and *EA* values and can be fruitful, in principle, for the evaluation of the reactivity of fullerene derivatives in electron transfer reactions in both the solution and gas phase.

In this work, based on our and published data, we show that the unique linear relationship E°_{red}—*EA* is suitable for fullerenes C_{60} and C_{70}, hydrofullerenes, fluorofullerenes, and several aromatic hydrocarbons.

Table 1. Reduction potentials (E°_{red}) and electron affinity (*EA*) for fullerenes, their functional derivatives, and aromatic hydrocarbons

No	Compound	Solvent	E°_{red}/V ($Fc^{0/+}$)	*EA* /eV	Reference	
					E	*EA*
1	C_{60}	CH_2Cl_2	−1.04	2.65	2	13
2		THF	−0.86		2	
3		TCE[a]	−1.06		11	
4		DMF	−0.77		12	
5	C_{70}	CH_2Cl_2	−0.97	2.72	2	13
6		THF	−0.85		2	
7		TCE[a]	−1.02		11	
8		DMF	−0.77		12	
9	$C_{60}F_{36}$	CH_2Cl_2	−0.21	3.48	14	14
10	$C_{60}F_{46}$	CH_2Cl_2	0.35	4.23	14	14
11	$C_{60}F_{48}$	CH_2Cl_2	0.37	4.06	14	14
12	$C_{60}F_{48}$	CH_2Cl_2	0.34	4.06	15	16
13	$C_{70}F_{54}$	CH_2Cl_2	0.53	4.42	14	14
14	$C_{60}H_{36}$	THF	−3.18	$-(0.24\pm0.03)^b$	7	17
15	Anthracene	THF	−2.57	0.57	7	18
16	Naphthalene	DMF	−2.93	0.15	19	18
17	C_6H_6	THF	−3.81	−1.1	9	18
18	$C_{60}H_{18}$		$-1.74\div-1.91^c$	1.4—1.6		10
19	$C_{70}H_{36-38}$	THF	−3.16	-0.15^c	8	
20	$C_{70}H_{44-46}$	THF	−3.37	-0.41^c	8	
21	$C_{60}H_2$	CH_2Cl_2	−1.11	2.45^c	20	
22		Benzonitrile	−1.04		20	
23		Toluene/DMF	−1.02		12	
24	$C_{70}H_2$	Toluene/DMF	−1.04	2.47^c	12	

[a] In 1,1,2,2-tetrachloroethane.
[b] Theoretical value.
[c] This work.

Results and Discussion

The known E°_{red} values in various media and *EA* in the gas phase for fullerenes C_{60} and C_{70}, their hydro- and fluoro-derivatives, and several of aromatic hydrocarbons are collected in Table 1. The values were generalized on the basis of our[7—10] and published data.[2,11—20] The $E^\circ_{red} = (E_p{}^c + E_p{}^a)/2$ values were measured by cyclic voltammetry ($E_p{}^c$ and $E_p{}^a$ are the potentials of the cathodic and anodic peaks, respectively) and are presented against the $Fc^{0/+}$ redox pair (Fc is ferrocene) used as the reference electrode.*

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* For data[11—15] where other reference electrodes were used, we performed the corresponding recalculation of E°_{red}.

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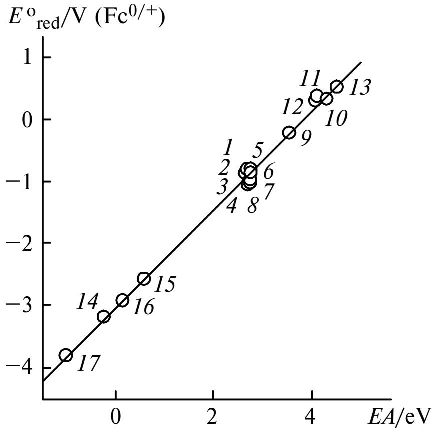

Fig. 1. Linear relationship between the first reduction potentials and electron affinity in the gas phase for fullerenes, their functional derivatives, and aromatic hydrocarbons ($r^2 = 0.997$). Figures correspond to numbers in Table 1.

The $E°_{red}$—*EA* plot is presented in Fig. 1. The unique linear relationship of these values is observed for both fullerenes and their derivatives and aromatic hydrocarbons. The plot of $E°_{red}$ *vs.* *EA* (Fig. 1) can be presented in the analytical form by the equation

$$E°_{red} \text{ (V } vs. \text{ Fc}^{0/+}) = -(3.04\pm0.04) + (0.81\pm0.02)\cdot EA. \quad (2)$$

This linear relationship with the correlation coefficient $r^2 = 0.997$ is fulfilled even without a correction of the $E°_{red}$ values by the $\Delta\Delta G_{sol}$ value. It can be assumed that this is a result of close $\Delta\Delta G_{sol}$ values for fullerene derivatives and aromatic hydrocarbons in spite of the fact that $E°_{red}$ were measured in different solvents (see Table 1). Note that, according to published data,[5] the relationship in DMF has the form

$$E°_{red} \text{ (V } vs. \text{ SCE)} = -(2.95\pm0.06) + EA,$$

and $\Delta\Delta G_{sol}$ for fullerenes C_{60}—C_{86}, $C_{60}F_{48}$ and aromatic hydrocarbons are (−1.76±0.06) and (−1.99±0.05) eV, respectively, *i.e.*, they are rather comparable. In addition, according to Ref. 5, $\Delta\Delta G_{sol}$ for fullerenes and their derivatives is minimum* compared to those of aromatic hydrocarbons and metal complexes and has close values in different solvents (for example, (−1.76±0.06) eV in DMF and (−1.53±0.06) eV in CH_2Cl_2), which is explained by the large rigid skeleton in fullerene molecules and results in the maximum charge delocalization in fullerene anions. In our opinion, the main reason for the existence of the unique linear relationship (2) is the fact that MO of the fullerene skeleton make the greatest contribution, most likely, to LUMO of fullerenes and their derivatives (MO to which an electron is transferred during reduction).

Equation (2) does not confine the class of compounds for which this relationship is fulfilled. It is only significant that the $\Delta\Delta G_{sol}$ values for these classes would be close in magnitude because Eq. (2) was obtained ignoring the correction of $E°_{red}$ by the $\Delta\Delta G_{sol}$ value. This condition is fulfilled, in principle, for fullerene derivatives **9—14** and aromatic hydrocarbons **15—17** presented in Table 1 (see above and Ref. 5) and, hence, the data for these compounds obey excellently ($r^2 = 0.997$) the rectilinear plot (2) (see Fig. 1).

As it should be expected, the slope of the linear plot is close to unity (0.81). The slope somewhat lower than 1 can be explained, for example, by the fact that the $E°_{red}$ values for the compounds indicated in Table 1 in various solvents ignoring the correction of $E°_{red}$ by the $\Delta\Delta G_{sol}$ value. According to published data,[5] for fullerenes C_{60}—C_{86} and $C_{60}F_{48}$, aromatic hydrocarbons, metalloporphyrins, and acetylacetonate metal complexes for which the $E°_{red}$ values were measured in one solvent (DMF) and $E°_{red}$ was corrected taking into account $\Delta\Delta G_{sol}$, the slope of the slope linear relationship is 1. If we specify the slope also equal to 1, then, taking into account the 95% confidence interval, the correlation coefficient is the same 0.997, and the analytical form of the relationship can be described by the equation $E°_{red} = -(3.51\pm0.08) + EA$.

Using equation (2) and experimental $E°_{red}$ value, we can predict the unknown *EA* value for fullerene derivatives and *vice versa*. For example, for $C_{60}H_2$, depending on the medium, the measured $E°_{red}$ value varies within −1.02—−1.14 V ($Fc^{0/+}$),[12,20] which allows the estimation of the unknown *EA* value as 2.38—2.49 eV (average value (2.45±0.04) eV). Similarly, using the known value $E°_{red} = -1.04$ V ($Fc^{0/+}$), for $C_{70}H_2$ this estimation gives $EA = (2.47\pm0.04)$ eV. By contrast, for $C_{60}H_{18}$ the estimate of *EA* is known (1.4—1.6 eV),[10] which was determined experimentally by the mass spectrometric study of negative molecular ions $C_{60}H_{18}{}^{\bullet-}$. Then the unknown $E°_{red}$ value for this hydrofullerene should be −1.74 to −1.91 V ($Fc^{0/+}$). Finally, for $C_{70}H_{36-38}$ and $C_{70}H_{44-46}$ (reduction is irreversible) $E°_{red} = -3.16$ and −3.37 V ($Fc^{0/+}$), respectively,[8] which allows the estimation of the *EA* values for these hydrofullerenes as approximately −(0.15±0.04) and −(0.41±0.04) eV (see Table 1).

Taking into account these data and those presented in Table 1, it is evident that with an increase in the number of H atoms in hydrofullerenes the $E°_{red}$ values are shifted to the region of negative potentials (reduction becomes more difficult) and the *EA* values decrease.

Thus, along with the relationships $E°_{red}$—energy level of LUMO (see, *e.g.*, Ref. 22), the unique linear relationship between $E°_{red}$ and *EA* values for fullerenes and their derivatives found in this work allows the prediction by Eq. (2) of one of these values if another value is experimentally measured. It is substantial that $E°_{red}$ values can be determined with a good accuracy (±0.01 V),[23] and their measurement requires only ≤1 mg of the analyzed substance. Therefore, the estimation of *EA* by the experimental $E°_{red}$ values is especially attractive.

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* $\Delta\Delta G_{sol}$ decreases with an increase in the molecule size.[21]

In conclusion note that a linear relationship should also be fulfilled, in principle, between oxidation potentials (E_{ox}) of fullerenes and their derivatives and ionization potentials (IP) of these compounds in the gas phase because an electron is removed from HOMO during both electrooxidation and ionization.[21] This relationship would allow the prediction of E_{ox} or IP values having experimentally measured only one of them. In addition, when E_{red} and E_{ox} are known, we can calculate the electrochemical gap $G = E_{ox} - E_{red}$ (analog of the energy gap HOMO—LUMO) and electrochemical electronegativity $\chi = (E_{ox} + E_{red})/2$ (see Refs. 24 and 25), which characterize quantitatively the "rigidity" and reactivity of fullerenes and their derivatives in redox reactions, as we have performed this previously[7,8] for hydrofullerenes $C_{60}H_{36}$ and $C_{70}H_{36-46}$. The general tendency of changing the reactivity of these compounds in reactions accompanied by electron transfer can be prognosticated, in principle, by a change in the G value in the series of fullerene derivatives. Unfortunately, a few number of reliable IP values for fullerene derivatives does not allow yet this prognosis to be made.

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