Redox-induced hydrogen transfer from hydrofullerene $C_{60}H_{36}$ to fullerene C_{60}

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The possibility of hydrogen transfer from hydrofullerene $C_{60}H_{36}$ to electrogenerated radical anion $C_{60}{}^{\cdot -}$ or dianion $C_{60}{}^{2-}$ in propylene carbonate—toluene (3 : 2, v/v) was demonstrated by cyclic voltammetry. The process affords $C_{60}H_2$ as the product. The reaction found is the typical redox-induced process.

Key words: fullerenes, C_{60}, hydrofullerenes, $C_{60}H_{36}$, $C_{60}H_2$, hydrogen transfer, redox-induced reactions, cyclic voltammetry.

The fact of a substantial increase in reactivity of organic, organometallic, and coordination compounds during their redox activation is well known.[1–6] First, the electron transfer to the antibonding orbital results in weakening of bonds in the activated molecule. Second, the reductive activation increases the basicity of the substrate, which also increases its reactivity. Third, the radical states generated are more reactive than the initial states. As a result, radicals, radical anions, and anions participate in the reactions, which is hardly possible or do not occur at all for their neutral precursors. In addition, the reactions typical of both ground and reduced states of the substrates occur, in the latter case, with rates higher by many orders of magnitude.[4–6]

In this work, studying the reduction of C_{60} in a solution of the electrolyte (propylene carbonate—toluene (3 : 2, v/v)—0.05 *M* Bu_4NPF_6) in the presence of hydrofullerene $C_{60}H_{36}$, we found a new redox-induced reaction of hydrogen transfer from hydride to fullerene.

When carbon fibers obtained from pyrolyzed polyacrylonitrile (PPAN)* are used as the working electrode, the $C_{60}H_{36}$ hydride itself is electrochemically inactive in the operating interval of potentials (from +0.5 to −2.5 V relative to the internal standard $Fc^{0/+}$, where Fc is ferrocene). When fullerene C_{60} (for example, an equimolar amount) is added to the solution, and the electrode potential is cycled for a long time (1—2 h at v = 0.1 V s^{-1}), in an electrolyzer without a diaphragm, the signals in the region of the first two redox transitions $C_{60}{}^{0/\cdot -/2-}$ decrease gradually, and new peaks appear. A similar result was obtained for potentiostatting of the PPAN electrode at the potentials of the limiting current of the second redox transition $C_{60}{}^{\cdot -/2-}$. The color of the electrolyte solution initially caused by fullerene (magenta) changes to brown with the simultaneous formation of a precipitate with the same color. The precipitate is insoluble in standard solvents (toluene, acetone, alcohols, and others) and in CS_2, while hydride $C_{60}H_{36}$ is soluble[7] mainly in CS_2, which indicates the polymeric character of the residue. The IR spectra of the residue, which was successively washed with toluene and acetone and dried *in vacuo* (100 °C, 4 h), contain absorption bands (AB) at 2917, 2853, 1793, 1708, 1674, 1628, 1494, 1456, 1429, 1333, 1318, 1263, 1240, 1177, 939, 922, 817, 731, 693, 669, 581, 566, 528, and 484 cm^{-1}. This indicates that the residue consists of both fragments of hydrofullerenes C_{60} (intense AB of stretching vibrations of C—H at 2917 and 2853 cm^{-1} characteristic of hydrofullerenes with a high content of hydrogen[7]) and fragments of fullerene and/or its derivatives with a low degree of functionalization (AB at 1429, 1177, 581, and 528 cm^{-1}, the majority of which is shifted relative to AB at 1429, 1183, 576, and 527 cm^{-1}, which are characteristic of pure C_{60}, with a change in the ratio of their intensities[8]). At the same time, after electrolysis of the electrolyte solution, its spectrum in the visible region exhibits AB with λ = 332, 406, 434, 592 (sh), and 702 (sh) nm, which indicates that both the starting fullerene (406 and 592 nm), and hydride $C_{60}H_2$ (the hypsochromic shift of the absorption band of C_{60} at λ = 336 nm by 4 nm and the appearance of new bands at 434 and 702 nm inherent in this hydrofullerene[8]) are present in the solution. According to the data of spectrophotometric analysis, the conversion of fullerene C_{60} to $C_{60}H_2$ and products in the residue is not less than 50%. The composition of the residue is presently under more detailed study.

As we have shown previously,[9] the electropolymerization of C_{60} occurs in parallel on the PPAN

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* PPAN was chosen as the working electrode because of the highly developed surface of this material, which is very important when electron transfer-induced reactions are performed in the preparative scale.

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electrode to form a film of electroactive poly-C_{60}, the signals from which prevent identification of products formed from C_{60} and $C_{60}H_{36}$ in the solution. Therefore, to record cyclic voltammograms, the working PPAN electrode was replaced after the electrolysis with a new one. In the typical experiment (Fig. 1), after the replacement of the PPAN electrode, the voltammograms contain the peaks of fullerene ($E^0_{1,2} = (E_p^c + E_p^a)/2 = -0.96$ and -1.39 V (*vs.* to $Fc^{0/+}$), where E^0_1 and E^0_2 are the formal standard potentials of the redox pairs $C_{60}^{0/\cdot-}$ and $C_{60}^{\cdot-/2-}$, E_p^c and E_p^a are the potentials of the cathodic and anodic peaks, respectively), and a more cathodic peak with the corresponding anodic response ($E^0_1 = -1.13$ V, $Fc^{0/+}$) appears in the region of the first peak. According to the published data,[10,11] this new pair of peaks should be referred to the redox transition $C_{60}H_2^{0/\cdot-}$ (the value $E^0_1 = -1.14$ V, $Fc^{0/+}$, has been previously determined[10] in the toluene—DMSO (2 : 1, v/v) medium). This indicates unambiguously that *hydrogen is transferred to fullerene during the electron transfer-induced reaction between C_{60} and $C_{60}H_{36}$*. It should be mentioned that under other equivalent conditions (temperature, medium, concentrations of reagents, reaction time, *etc.*), but in the absence of the current, the reaction between C_{60} and $C_{60}H_{36}$ does not proceed. For example, according to the data of spectrophotometric monitoring, the concentration of C_{60} in the reaction mixture without electrode polarization remains unchanged, while during potential cycling in the region of the $C_{60}^{0/\cdot-/2-}$ redox transition or potentiostatting of the electrode in the region of potentials of the C_{60}^{2-} dianion generation, the concentration of fullerene in the electrolyte solution decreases noticeably with the simultaneous increase in the concentration of $C_{60}H_2$.

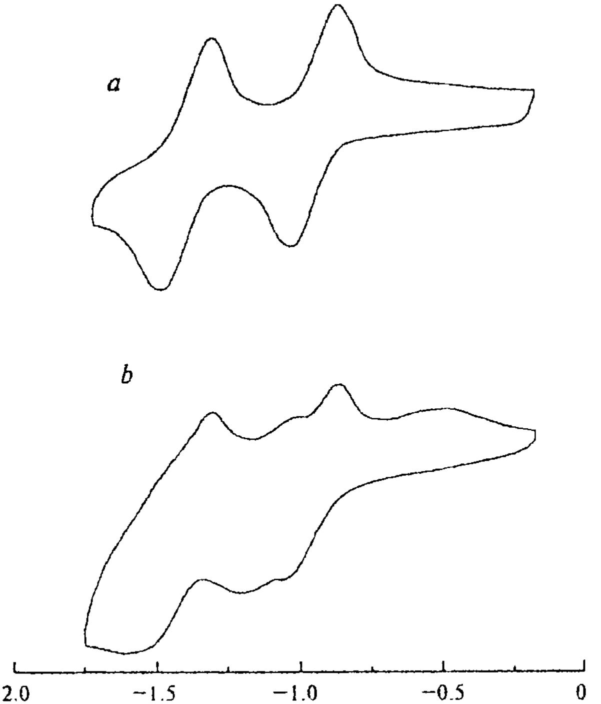

Fig. 1. Cyclic voltammograms in the polyscan regime: *a*, fullerene C_{60} ($2.3 \cdot 10^{-4}$ mol L^{-1}) in the propylene carbonate—toluene (3 : 2, v/v)—0.1 *M* Bu_4NPF_6 solution on the PPAN electrode ($v = 0.1$ V s^{-1}) at ~20 °C; *b*, the same but after preliminary potentiostatting of the PPAN electrode at $E = -1.75$ V ($Fc^{0/+}$) for 1 h, replacement of the PPAN electrode with a new one, and addition of $C_{60}H_{36}$ (~$2.4 \cdot 10^{-4}$ mol L^{-1}) to the electrolyte solution. Some difference in heights of the peaks is due to the use of PPAN electrodes with different surface areas. The nature of the peak designated by the asterisk is presently unknown.

It is known[10,12] that hydride $C_{60}H_2$ is a sufficiently strong CH-acid ($pK_1 = 4.7$, $pK_2 = 16$). Experimental data on the acidity of $C_{60}H_{36}$ are unknown, although the quantum-chemical calculations show[13] that the acidity of hydrofullerenes decreases as the number of hydrogen atoms in the molecule increases, and for $C_{60}H_{36}$, pK_1 is equal to 31.35. It is clear that for these ratios of p*K* values, deprotonation of $C_{60}H_{36}$ under the action of the electrogenerated C_{60}^{2-} dianion is unreal. Then the elimination of the H atom from hydrofullerene $C_{60}H_{36}$ by the radical anion or dianion of C_{60} is the single possibility, in our case, to form $C_{60}H_2$. Presently, it is impossible to conclude unambiguously which species ($C_{60}^{\cdot-}$ or C_{60}^{2-}) reacts. For example, the formation of $C_{60}H_2$ (although in somewhat less amounts) is observed in the C_{60}—$C_{60}H_{36}$ mixture at the potentials of $C_{60}^{\cdot-}$ generation under other equivalent conditions (time of electrolysis, concentrations of reagents, *etc.*). Of course, $C_{60}^{\cdot-}$ can disproportionate to C_{60} and C_{60}^{2-}, which participates in the formation of $C_{60}H_2$. The value of the equilibrium constant of the disproportionation of $C_{60}^{\cdot-}$ (*K*) can be estimated from the known equation[14]

$$\log K = F(E^0_2 - E^0_1)/(2.303RT),$$

where *F* is Faraday's number. This constant is ~10^{-7}, which is small; however, the possibility of the participation of $C_{60}^{\cdot-}$ in the elimination of the H atom from $C_{60}H_{36}$ to form $C_{60}H_2$ cannot be ruled out.

In order to estimate the possibility of the formation of $C_{60}H_2$ from $C_{60}H_{36}$, we also calculated the C—H bond energies in these hydrofullerenes. The value of the C—H bond energy was estimated from the thermodynamic cycle:

$$C_{60} + nH_2 = C_{60}H_{2n}, \qquad \Delta H_1, \tag{1}$$

$$nH_2 = 2nH, \qquad n\Delta H_2, \tag{2}$$

$$C_{60}H_{2n} = C_{60} + 2nH, \qquad \Delta H_3, \tag{3}$$

where ΔH_1 is the standard enthalpy of reaction (1) equal to -525.5 and -36.9 kcal mol^{-1} for $n = 18$ and 1, respectively (taken from the theoretical work[15]), and $\Delta H_2 = 104.2$ kcal mol^{-1} is the enthalpy of dihydrogen dissociation to atoms. By the C—H bond energy we mean the enthalpy of reaction (3), ΔH_3, referred to the number of hydrogen atoms in hydrofullerene. The C—H bond energies thus calculated were equal to 66.7 and 70.5 kcal mol^{-1} for $C_{60}H_{36}$ and $C_{60}H_2$, respectively. The comparison of these values shows that the cleavage of the C—H bond in $C_{60}H_{36}$ followed by the formation of the C—H bond in $C_{60}H_2$ is energetically favorable, and this reaction can be performed in practice.

Presently, it is not reasonable to present in detail the mechanism of formation of $C_{60}H_2$, because subsequent transformations of the primary product of the elimination of the H atom from hydrofullerene $C_{60}H_{36}$ are unknown. Nevertheless, during potential cycling, the voltammograms of the C_{60}—$C_{60}H_{36}$ mixture exhibit isopotential points (they are not presented in Fig. 1), which are analogs of isobestic points in spectrophotometry. These points favor the quantitative transformation of the electrogenerated C_{60}^{2-} dianion or $C_{60}^{\cdot -}$ radical anion into $C_{60}H_2$ (the kinetics of this process is presently under study). We believe that the radical products obtained from hydrofullerene $C_{60}H_{36}$ undergo subsequent chemical transformations into insoluble compounds, probably, with a polymeric structure, which precipitate. The formation of the precipitate due to parallel anodic processes involving C_{60} and/or $C_{60}H_{36}$ should not be considered, since the precipitate appears when the reaction is performed in electrolyzers both without and with a diaphragm.

The further hydrogenation of $C_{60}H_2$ by the hydrogen transfer from $C_{60}H_{36}$ to electrogenerated $C_{60}H_2^{\cdot -}$ or $C_{60}H_2^{2-}$ is improbable, because, as has been shown previously,[11] these species are unstable even in the time scale of cyclic voltammetry and decompose rapidly to form C_{60}.

Experimental

Fullerene was prepared and purified by the previously described procedure.[16] Propylene carbonate (pure grade) was distilled under reduced pressure (10 Torr), exposed for 1 day over molecular sieves 4A, and again distilled *in vacuo*. Toluene (pure grade) was dehydrated above calcined $CaCl_2$ and twice distilled above sodium. All purified solvents were stored under an atmosphere of dry argon.

Electrochemical measurements were carried out, as described previously,[17] at ~20 °C in a dry inert atmosphere in the propylene carbonate—toluene (3 : 2, v/v)—0.1 *M* Bu_4NPF_6 mixture in a sealed three-electrode electrochemical cell with nonseparated or separated (a graphite rod sealed into glass) cathodic and anodic spaces. Tetrabutylammonium hexafluorophosphate (Aldrich) was used without additional purification.

All potentials were determined relative to the reference electrode $Fc^{0/+}$ (E^0 = +0.43 V *vs.* to the saturated calomel electrode) by the addition (at the end of each experiment) of ferrocene to the testing solution and measurement of potentials of peaks under study relative to the reversible potential of the ferrocene/ferrocenium pair. The reference electrode was a Ag/AgCl/4 *M* aqueous solution of LiCl separated from the solution studied in the cell by a bridge filled with a solution of the supporting electrolyte. A platinum wire served as the auxiliary electrode. Carbon fibers of pyrolyzed polyacrylonitrile (PPAN) were used as the working electrode (according to the X-ray photoelectron spectroscopic data, the content of nitrogen in the fibers is ~1.5%). Voltammetric measurements and electrolysis with controlled potential were carried out using a PR-8 programmer and a PI-50-1 potentiostat without additional compensation of ohmic losses. Voltammograms were recorded on an N307/1 two-coordinate automatic recorder.

IR spectra were recorded on a Perkin Elmer-2000 IR-Fourier spectrometer (resolution 2 cm^{-1}, pellets with KBr), and electronic spectra were recorded on a Specord M-40 instrument (resolution 1 nm).

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