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Fullerene hydrides: synthesis, properties, and structure

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Abstract. The results of studies on the methods of synthesis of exohedral fullerene hydrides, including the reduction of fullerenes by hydrocarbons, the catalytic hydrogenation of fullerenes, *etc*., are surveyed. Much attention is devoted to the state of hydrogen in solid fullerene hydrides, the structure of fullerene hydrides, and their reactivity. The bibliography includes 148 references.

I. Introduction

Fullerenes are unique molecules, the reactivity of which has been the object of numerous studies (see, for example, Refs 1 – 4). Early studies revealed that C_{60} exhibits a high reactivity in relation to nucleophiles,[1,5–9] free radicals,[4,10] and the halogens[11] and it participates in cycloaddition reactions, including the photocycloaddition of anthracene.[12] These reactions usually result in the formation of a set of products which are difficult to separate and which retain the spherical C_{60} structure. The selective reactions include the osmylation reactions[13] and the synthesis of fullerene epoxides[14–16] and fulleroids containing the diphenylmethylene fragment.[17] The reactions involving the addition of metal complexes to C_{60} and C_{70} are controlled by the stoichiometry of the process and the steric loading of the complex.[18–20] The formation of complexes between fullerenes and low-valence electron-donating metal centres, such as $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$, $[(Et_3P)_2M]_6(\eta^2\text{-}C_{60})$ (M = Pt, Ni) $(\eta^2\text{-}C_{60})IrCl(CO)(PPh_3)_2 \cdot 5C_6H_6$, $(\eta^2\text{-}C_{60})RhH.(CO)(PP_3)_2$, $(\eta^2\text{-}C_{60})Ru(CO)_4$, *etc*., in which fullerene acts as a η^2-ligand, indicates that the double bonds of the fullerene skeleton are electron-deficient. Thus the degree of electron transfer from the metal in the adduct $(\eta^2\text{-}C_{60})Ir(CO)Cl(PPh_3)_2$ is similar to that observed in the dioxygen complex $O_2Ir(CO)Cl(PPh_3)_2$.[21] Calculations of the electronic structure of C_{60}[23,24] confirmed that the π-system of the molecule is electron-deficient and that fullerene behaves like a polyolefin rather than an aromatic compound.

The C_{60} structure (I_h symmetry) contains C – C bonds of two types: the shorter double bonds forming common sides of two hexagons (henceforth referred to as the 6 – 6 bonds)† and the longer single bonds, constituting the common side of a hexagon and a pentagon (the 6 – 5 bonds).[25,26] In the C_{70} structure (D_{5h} symmetry), there are five types of carbon atoms and correspondingly eight distinct types of C – C bonds. Four of these constitute the common sides of hexagons, while the other four are formed when five- and six-membered rings fuse.[20] Fig. 1 presents the lengths of the 6 – 6 and 6 – 5 bonds in the C_{60} molecule, while Fig. 2 presents schematic Schlegel diagrams for C_{60} and C_{70}.[27] In the C_{60} and C_{70} fullerenes, the 6 – 6 bonds are the most reactive and addition to these bonds occurs when fullerenes interact with transition metal complexes (see, for example, Refs 18 – 22).

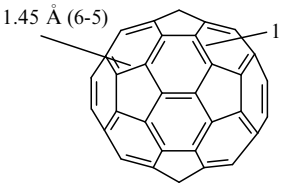


Figure 1. The lengths of the 6 – 5 and 6 – 6 bonds and their positions in the C_{60} molecule.

The simplest method for the chemical modification of fullerenes is the hydrogenation of double bonds. The reduction of fullerenes is of great interest because they can serve as an effective medium for the storage of hydrogen.[28] Theory predicts that hydrogen atoms may be located both within (endohedrally) and outside (exohedrally) the fullerene spherical surface and that a stable $C_{60}H_{60}$ isomer can be obtained only if ten hydrogen atoms are bound endohedrally in the molecule. Traditional methods of organic chemistry are used in the chemistry of fullerenes for the synthesis of a wide variety of compounds, including hydrogenated derivatives.

The aim of the present review is a survey of the available literature data on the methods of synthesis and studies on the structures and reactivities of exohedral fullerene hydrides. There exist several reviews and monographs in which the problem of the hydrogenation of new carbon clusters is dealt with (see, for example, Taylor and Walton[2] and Hirsch[3]), but the rapid development of research in this field requires its special consideration and systematic treatment.

II. Methods of synthesis of fullerene hydrides

1. Birch reduction of fullerenes

The C_{60} fullerene can be reduced by the Birch – Hückel method. According to thin-layer chromatographic data, the reduction produces a single compound (TLC, CH_2Cl_2 : hexane = 1 : 3, R_f = 0.37).[29] On heating, the substance obtained (white or cream coloured) began to darken at 170 °C but did not melt up to 305 °C.

$$C_{60} \xrightarrow{Li,\ NH_3(l),\ Bu^tOH} C_{60}H_{2n}\,.$$

† For the numbering of the atoms, see Taylor.[27]

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Table 1. Reduction of the C_{60} and C_{70} fullerenes.

System [a]	Substrate : reagent (substrate : reagent : catalyst)	Reaction conditions			Mass spectrometric method [b]	Reaction product [c]	Physicochemical characteristics of fullerene hydrides			Ref.
		T /°C	time /h	P_{H_2} /atm			UV and visible spectra, λ /nm (solvent)	IR, ν /cm^{-1} (assignment)	^{1}H NMR, δ /ppm (solvent)	
A. Reduction of C_{60} fullerene										
C_{60}–Li–NH_3(l)–Bu^tOH		−78			EI-MS	$C_{60}H_{36}$, $C_{60}H_{18}$	222 (cyclohexane)	2925, 2855 (C–H), 1620, 1450, 1400, 675	2.5–4.2 with maxima at δ = 3.8 and 3.35 ($CDCl_3$)	29
C_{60}–Li–NH_3(l)–THF–Bu^tOH		−78			L^2TOF-MS, ICR-MS, SIMS	$C_{60}H_{18}$–$C_{60}H_{32}$				30
C_{60}–BH_3·THF	1 : 1	5	0.75		FAB-MS	$C_{60}H_2$	207.5, 254, 324, 435 (hexane)	1426, 1178, 860 575.5, 574, 566, 552, 550, 545.5, 531.5 and 526.5, 522.5, 517	5.93 (toluene-d_8)	33
$C_{60}H_2$–BH_3·THF	1 : 1	0	0.75		FAB-MS	6 isomers of $C_{60}H_4$ (1,2,3,4-$C_{60}H_4$ — 50%)	342 sh, 442 (toluene : hexane = 1 : 1)			42
C_{60}–N_2H_2	1 : 1000	20	19			1,2-$C_{60}H_2$ (11), 1,4-$C_{60}H_2$ (5), 1,2,18,36-$C_{60}H_4$ (1.5), 1,2,3,4-$C_{60}H_4$ (10.5)			6.97 (CS_2); 5.89 (C_6D_6) 7.23 (CS_2); 6.13 (C_6D_6) 6.38 (CS_2); 5.49 (C_6D_6) 5.72 (CS_2); 4.56 (C_6D_6)	38
C_{60}–DHA	1 : 120	350	0.5		FD-MS, FAB-MS, EI-MS	$C_{60}H_{36}$	230 (CH_2Cl_2)	2913, 2850 (C–H), 1733, 1606, 1511, 1257, 1198, 1169, 1076, 745	2.5–4.2 with maxima at 3.3, 3.7, and 4.0 ($CDCl_3$)	45
C_{60}–DHA-d_4	1 : 120					$C_{60}D_{36}$		2128 (C–D)		45
C_{60}–DHA	1 : 120	350	24		FD-MS, FAB-MS, EI-MS	$C_{60}H_{18}$		2925, 2897, 2854 (C–H)		45
C_{60}–DHA–K	(1 : 100 : 5)	250	2		EI-MS	$C_{60}H_x$ (x = 0–36, 42–44)		2962, 2921, 2853 (C–H)	3.00–4.70 with maxima at 4.43, 4.28, 4.20, 4.00, 3.86, 3.45 ($CDCl_3$)	47
C_{60}–DHA-d_4–K-d_2	(1 : 100 : 5)	250	4.5			$C_{60}D_x$ (x = 0–36)		2153 (C–D)		47
C_{60}–H_2		300–350		500–850	ICR-MS	$C_{60}H_x$ (x = 2–18) [d]				59
C_{60}–H_2–C_2H_5I		400		70	FAB-MS	$C_{60}H_{36}$		2912, 2847, 2827 (C–H), 1655, 1460, 1025, 669		61
C_{60}–H_2–Pd/C (Pt/C)		180		100	FD-MS	$C_{60}H_{36}$, $C_{60}H_{18}$		2918, 2858 (C–H)	2.5–4.5($CDCl_3$)	80, 81
C_{60}–H_2–5% Ru/C		180	2	110	FD-MS	$C_{60}H_{36}$, $C_{60}H_{38}$, $C_{60}H_{40}$, $C_{60}H_{42}$	220 (cyclohexane)		2.1–4.25	83
C_{60}–H_2–5% Ru/C		180	2	130	FD-MS	$C_{60}H_{42}$, $C_{60}H_{46}$				83

Table 1 (continued).

System [a]	Substrate : reagent (substrate : reagent : catalyst)	Reaction conditions			Mass spectrometric method [b]	Reaction product [c]	Physicochemical characteristics of fullerene hydrides			Ref.
		T /°C	time /h	P_{H_2} /atm			UV and visible spectra, λ /nm (solvent)	IR, ν /cm^{-1} (assignment)	^{1}H NMR, δ /ppm (solvent)	
$C_{60}-H_2-5\%$ Ru/C		280	24	120	FD-MS	$C_{60}H_{42}$, $C_{60}H_{46}$				83
$C_{60}-H_2-5\%$ Ru/C		180	2	20–50	FD-MS	$C_{60}H_{18}$	220, 265 (cyclohexane)		3.0–4.5 ($CDCl_3$)	82
$C_{60}-Zn-$acid		110	6		FAB-MS	1,2-$C_{60}H_2$, $C_{60}H_4$, $C_{60}H_6$				55
$C_{60}-Zn-$conc. HCl		20	1.5		EI-MS	$C_{60}H_{36}$ (82%),	207, 257, 274.5 276.5, 283.5, 292.5, 300.5, 304.5, 307, 313, 317.5, 320.5, 329	2913, 2849 (C–H) 1725, 1635, 1456, 1384, 1273, 1123, 1073, 1035, 730, 678	2.5–4.2 with maxima at 2.55, 2.95, 3.05, 3.3, 3.5,3.9, 4.0	56
						$C_{60}H_{38}$ (15%), $C_{60}H_{40}$ (3%)				
$C_{60}-Zn-$conc. DCl					EI-MS	$C_{60}D_{36}$ (32%), $C_{60}D_{38}$ (31%), $C_{60}D_{40}$ (22%), $C_{60}D_{42}$ (11%), $C_{60}D_{44}$ (4%)				56
B. Reduction of C_{70} fullerene										
$C_{70}-BH_3\cdot$ THF	1 : 2	25			FAB-MS	7,8-$C_{70}H_2$, 1,9-$C_{70}H_2$	375, 410 (toluene–hexane) 355, 410 (toluene–hexane)		3.91 s (toluene-d_8)	43
$C_{70}-$DHA–K	(1 : 100 : 5)	250	2.5		EI-MS	$C_{70}H_x$ ($x = 0-36$)		2923, 2853 (C–H)	2.80–4.60	47
$C_{70}-$DHA-d_4–K-d_2	(1 : 100 : 5)	250	7		EI-MS	$C_{70}D_x$ ($x = 0-36$)		2150 (C–D)		47
$C_{70}-N_2H_2$	1 : 1000	20	19			7,8-$C_{70}H_2$ (1) 1,9-$C_{70}H_2$ (25)			4.96 (CS_2); 3.87 (C_6D_6) 5.32, 4.84 (CS_2); 4.22, 3.71 (C_6D_6)	38
						1,3,9,15-$C_{70}H_4$ (7) 1,5,6,9-$C_{70}H_4$ (9)			5.312, 4.859 (CS_2) 4.475, 4.127 (CS_2)	
$C_{70}-H_2-5\%$ Ru /C		100	2	2	FD-MS	$C_{70}H_2-C_{70}H_{18}$, $C_{70}H_{36}$ (traces)				84
$C_{70}-H_2-5\%$ Ru/C		180	2	20	FD-MS	$C_{70}H_{36}$	225 (C_6H_{12})		2.7–4.5 with maxima at 3.35, 3.8 and 4.0	84
$C_{70}-Zn-$conc. HCl		20	1.5		EI-MS	$C_{70}H_{36}$, $C_{70}H_{38}$	207, 223.5, 255, 259, 263, 269.5, 275.5, 278.5	2909, 2852(C–H), 1730, 1456, 1282, 1126, 1035, 750, 730, 695, 587, 468	2.4–4.0	56
					EI-MS	$C_{70}H_{40}$, $C_{70}H_{42}$ ($C_{70}H_{44}$)	295.5, 300, 303, 309.5, 312.5			
$C_{70}-Zn-$conc. DCl		20			EI-MS	$C_{70}D_{36}$, $C_{70}D_{42}-C_{70}D_{48}$				56

[a] Designations adopted for the reagents: DHA = dihydroanthracene, K = [7H]benzanthrene catalyst. [b] Designations adopted for the methods: EI-MS = mass spectrometry with sample ionisation by electron impact, L^{2}TOF-MS = laser desorption–laser ionisation time-of-flight mass spectrometry, ICR-MS = ion-cyclotron resonance mass spectrometry, SIMS = secondary ion mass spectrometry, FAB-MS = fast atoms bombardment mass spectrometry, FD-MS = mass spectrometry with field desorption. [c] The ratios of the reaction products are given in brackets. [d] Does not dissolve in the majority of organic solvents.

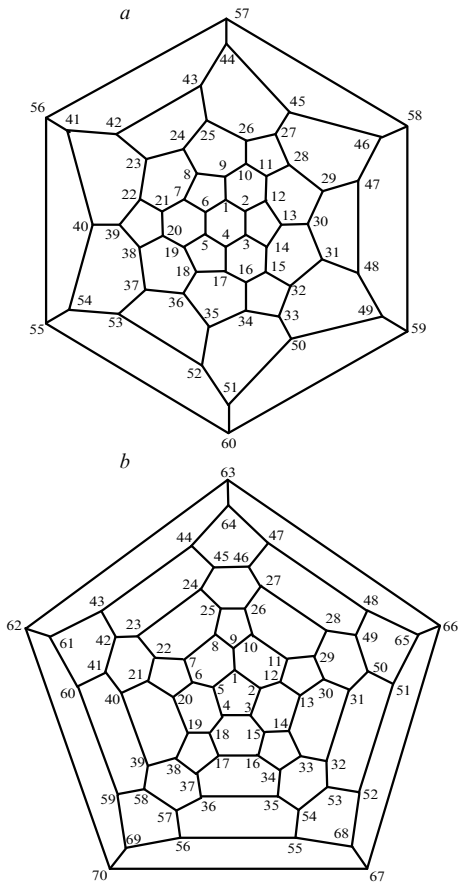


Figure 2. The Schlegel diagram for the C_{60} (*a*) and C_{70} (*b*) fullerenes with the numbering of the carbon atoms.[27]

Mass-spectrometric analysis with ionisation of the sample by electron impact (EI-MS) revealed the presence of two components with m/z 756 (M^+) and 378 (M^{2+}), as well as 738 (M^+) and 369 (M^{2+}), which agrees with the formulae $C_{60}H_{36}$ and $C_{60}H_{18}$ respectively (Table 1). $C_{60}H_{18}$ may be both the product of the direct reduction of C_{60} and the product of the pyrolysis of $C_{60}H_{36}$ formed in the course of the mass-spectrometric analysis. Thorough investigation of the initial reduction product using 'milder' mass-spectrometric methods showed that the Birch reduction leads to the formation of a mixture of polyhydrofullerenes $C_{60}H_{18}-C_{60}H_{36}$, the main product being $C_{60}H_{32}$.[30] This experimental distribution of C_{60} hydrides agrees well with the distribution of the products calculated by approximate methods on the assumption that the Birch reduction does indeed involve 1,4-hydrogen addition to the cyclohexadiene fragments of C_{60} (Table 2).[30]

Treatment of a toluene solution of the fullerene reduction product with a strong oxidant — 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) — leads to C_{60} on refluxing. Thus the reduction of C_{60} is fully reversible and the C_{60} skeleton does not break down in the course of the reaction.[29]

Under the conditions of the Birch reduction, the C_{70} fullerene affords $C_{70}H_{30}$ as the main product. It has been suggested that the most stable fullerene hydride is obtained as a result of the 1,4-addition of hydrogen to the double bonds on the C_{70} surface.[31]

Benzene may serve as the source of hydrogen in the reduction of fullerene by metallic potassium in the presence of crown–ethers (18-C-6).[32]

$$C_{60} + 3K + 18\text{-C-}6 \longrightarrow C_{60}^{3-} + 3\,K^+18\text{-C-}6,$$

$$C_{60}^{3-} + 2\,C_6H_6 \longrightarrow (C_{60}H_2)^{2-} + (C_{12}H_{10})^-.$$

Table 2. Experimental and calculated (numerical modelling of 1,4-addition by the Monte Carlo method) distributions of the products of the Birch reduction of C_{60}.[30]

Composition	Distribution of polyhydrofullerenes produced (% of main peak)	
	experiment [a]	calculation [b]
$C_{60}H_{24}$	39(24)	0.2
$C_{60}H_{26}$	53(35)	3
$C_{60}H_{28}$	72(57)	19
$C_{60}H_{30}$	96(89)	53
$C_{60}H_{32}$	100(100)	100
$C_{60}H_{34}$	71(62)	98
$C_{60}H_{36}$	11(10)	55
$C_{60}H_{38}$		14
$C_{60}H_{40}$		0.3

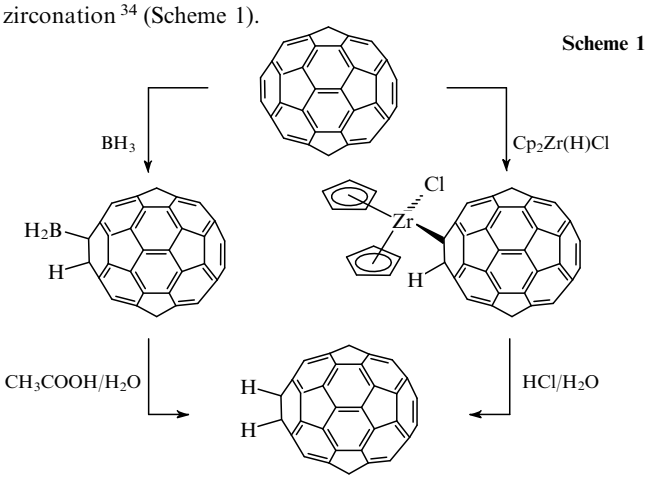
[a] The results of SIMS are quoted. The results of ICR-MS with laser desorption are given in brackets. [b] The calculation is based on the reduction of 20 000 C_{60} molecules.

2. Reduction of fullerenes by hydrides

The number of thermodynamically and kinetically stable isomers of the simplest fullerene hydrides ($C_{60}H_2$ and $C_{70}H_2$) is small.

Thus the reduction of C_{60} to $C_{60}H_2$ can lead to the formation of 23 isomeric dihydrides, two of which are the products of the 1,2- or 1,4-addition to the 6–6 bonds and have the lowest heats of formation, the latter isomer being less stable to the extent of 3.8 kcal mol^{-1}.[33] A two-stage process (the hydrometallation of C_{60} and C_{70} with subsequent hydrolysis), occurring with high regioselectivity, is a convenient method of synthesis of the lowest fullerene hydrides, which has been demonstrated in relation to the synthesis of $C_{60}H_2$ and $C_{70}H_2$ by hydroboration[33] or hydrozirconation[34] (Scheme 1).

Scheme 1

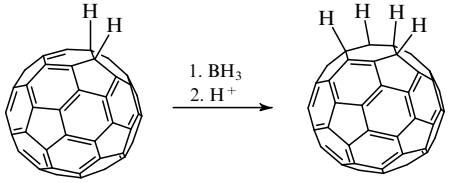


The interaction of C_{60} with $BH_3 \cdot THF$ in toluene at 5 °C (Table 1) with subsequent hydrolysis leads to a 10%–30% yield of $C_{60}H_2$ — the simplest fullerene hydride,[33] which was isolated with the aid of high performance liquid chromatography (HPLC). The formation of the stable $C_{60}H_2$ isomer is consistent with calculations.[35,37] The ^{1}H NMR spectra of $C_{60}H_2$ as well as $C_{60}HD$, prepared by the reaction of the intermediate $C_{60}HBH_2$ (Scheme 1) with CH_3COOD or D_2O, agree with the spectra of the products of the hydroalkylation of fullerene.[36] The regioisomer obtained is the product of 1,2-addition to the 6–6 bond. As in the case of 1-organo-1,2-dihydrofullerene,[36] the protons of the dihydrofullerene $C_{60}H_2$ give rise to a signal in the ^{1}H NMR spectrum at $\delta = 5.9$ ppm (toluene-d_8).[33] The second stable isomer ($\delta = 6.13$ ppm) was detected in this system in a significantly smaller amount.[38] The presence of a band at 430 nm in the electronic absorption spectrum of the brown solution of $C_{60}H_2$ is a characteristic property of C_{60} 1,2-adducts.[39] The interaction of C_{60} with an excess of $BH_3 \cdot THF$ and subsequent hydrolysis of the

resulting complex with either glacial CH_3COOH, $NaOH-H_2O_2$, or NaOH leads in the presence of atmospheric oxygen to the water-soluble fullerols $C_{60}(OH)_x$. When the IR spectra of the reaction products obtained under an inert atmosphere and in the presence of atmospheric oxygen were compared, it was found that the reaction proceeds via the oxidation of the C–H bonds in the hydrofullerene formed initially.[40] A similar process has been observed also in the reduction of C_{60} by tetrabutylammonium tetrahydroborate in benzene at room temperature.[41]

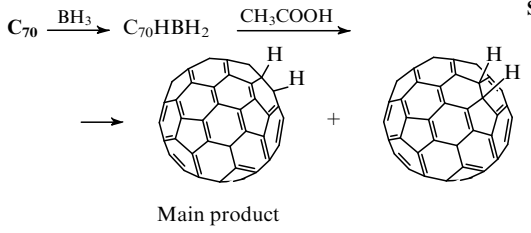
The hydroboration of the dihydride $C_{60}H_2$ (Scheme 2) leads to the formation of a mixture of six isomeric compounds $C_{60}H_4$ in ~10% yield, among which 1,2,3,4-$C_{60}H_4$ with all four hydrogen atoms added to neighbouring 6–6 bonds, is, according to ^{1}H NMR data, the main (~50%) reaction product.[42] It is also the thermodynamically most stable isomer.

Scheme 2



The interaction of C_{70} with $BH_3 \cdot THF$ (Table 1, Scheme 3) takes place, in contrast to C_{60}, at room temperature and leads to a ~20% yield of a mixture of 1,9- and 7,8-$C_{70}H_2$ in the ratio of 2 : 1, for which the difference between the free energies is $\Delta G_{295} = 1.4 \pm 0.2$ kcal mol^{-1}.[43]

Scheme 3



Main product

According to calculations,[37] the products of the 1,2-addition of H_2 to the 6–6 bond of the C_{60} and C_{70} fullerenes and the products of addition in the *para*-position in the six-membered ring have the lowest energy. Both $C_{70}H_2$ isomers isolated are the products of 1,2-addition. The 7,8- and 1,9-$C_{70}H_2$ isomers are not interconverted either on standing at room temperature for several weeks or on heating up to 100 °C for 1 h. However, in the presence of Pt/SiO_2 at room temperature, 7,8-$C_{70}H_2$ in solution in toluene is converted into a mixture consisting of the 7,8-$C_{70}H_2$, 1,9-$C_{70}H_2$ formed as a result of isomerisation, and C_{70} obtained on decomposition.[43] The 7,8-$C_{70}H_2$ isomer is less stable than the 1,9-isomer, but both are stable for a long time at −20 °C in toluene or hexane. Both substances are more sensitive to the action of light and air than $C_{60}H_2$.

The structures of the $C_{70}H_2$ isomers obtained have been confirmed by ^{1}H NMR spectra: the 7,8-$C_{70}H_2$ protons give rise to a singlet with $\delta = 3.91$ ppm, while the 1,9-$C_{70}H_2$ protons generate a quartet with the centre at 4.0 ppm. The electronic spectra of the $C_{70}H_2$ isomers differ appreciably from the absorption spectrum of C_{70} and may be useful for the identification of the C_{70} adducts.[43]

The interaction of organometallic compounds with fullerenes proceeds exclusively at the 6–6 bond.[18–22] Thus hydrozirconation opens a path to the selective synthesis of functional derivatives of fullerene. The product of the hydrozirconation of C_{60} is a zirconium(IV) complex, namely $[(\eta^5\text{-}C_5H_5)_2ZrCl]_nC_{60}H_n$, where $n = 1, 2$, or 3. Hydrolysis of this intermediate leads to a mixture of fullerene hydrides, among which the main product is $C_{60}H_2$ (Scheme 1).[34] The dihydride $C_{60}H_2$ obtained in this way has been characterised with the aid of ^{1}H NMR, IR and UV spectroscopy, and mass spectrometry.‡

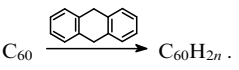
Other methods for the reduction of C_{60} and C_{70} fullerenes have also been described, for example reduction by hydrogen in the presence of 5% Pt/C, by Cr(II) acetate, and by diimide.[38] A change in the spectroscopic characteristics of the reaction mixtures in the visible region was noted in all cases. Peaks with $\delta = 5.9$ and 6.1 ppm were observed in the ^{1}H NMR spectra of C_{60} fullerenes. They refer to reduced C_{60} derivatives.[33,38] The fullerene derivatives obtained on treatment with Cr(II) acetate or with hydrogen in the presence of 5% Pt/C are unstable in the light; in the presence of atmospheric oxygen, they are converted into fullerols. On the other hand, the products of the reduction of C_{60} and C_{70} by diimide are formed in a high yield; the reaction is distinguished by its simplicity. This method is convenient for the synthesis of the di- and tetra-hydride derivatives of fullerenes.

$$C_{60} + H_2N_2 \longrightarrow C_{60}H_2 + N_2 .$$

The main product of the reduction of C_{60} by diimide is the 1,2,3,4-tetrahydrofullerene $C_{60}H_4$; apart from this compound, other $C_{60}H_4$ isomers and more highly hydrogenated compounds are also formed. When C_{70} was reduced with diimide, eight products were obtained: two of these were characterised as the tetrahydrides 1,5,6,9-$C_{70}H_4$ and 1,7,8,9-$C_{70}H_4$ and a further two were characterised as the dihydrides 1,9-$C_{70}H_2$ and 7,8-$C_{70}H_2$ identical to the compounds obtained previously by reduction with diborane.[43] It has been noted that the hydrogenated fullerene derivatives dissolve more effectively in CS_2 than in benzene or toluene. The chemical shifts of the ^{1}H NMR signals strongly depend on the solvent: in CS_2, they undergo a downfield shift (by 1 ppm) compared with benzene.

3. Reduction of fullerenes by hydrocarbons

At elevated temperatures, fullerenes serve as dehydrogenating agents in relation to hydrocarbons. Thus treatment of C_{60} in a sealed glass tube at 350 °C under an inert atmosphere with a melt of 9,10-dihydroanthracene (C_{60} : 9,10-DHA = 1 : 120), which serves as a source of hydrogen, leads to rapid (30 min) decolorisation of the melt.



It has been found that the reduction of the C_{60} fullerene under the conditions of the nonatalytic transfer of hydrogen atoms from the donor to the acceptor (transfer hydrogenation)[44] leads to the hydrides $C_{60}H_{36}$ and $C_{60}H_{18}$.[45] In this reaction, fullerene can function as a radical trap.[46]

After the sublimation of the excess DHA and of the anthracene produced, a white (or slightly yellowish) solid product $C_{60}H_{36}$ was isolated and was characterised by mass spectrometry. A peak at m/z 756 corresponds to it. The increase in reaction time to 24 h leads to the formation of a coloured product with m/z 738, which corresponds to the compound $C_{60}H_{18}$. The presence of a hydride having this composition has also been confirmed by thin-layer chromatography.§ At the same time the free C_{60} fullerene was detected in the melt. EPR study of this reaction showed that the 9-hydroanthryl radical is formed as an intermediate. $C_{60}D_{36}$ and $C_{60}D_{18}$ are formed similarly when dihydroanthracene-d_4, deuterated in the 9- and 10-positions, is used for the reduction of fullerene. Cyclohexa-1,4-diene has been used in the hydrogenation of C_{60} by the method of transfer hydrogenation.[45]

Solutions of $C_{60}H_{36}$ in a series of organic solvents are unstable even under an inert gas atmosphere. After a time, they become turbid and the signals in the ^{1}H NMR spectrum become broadened. Heating of the hydrides $C_{60}H_{36}$ and $C_{60}H_{18}$ in an inert gas (550 °C, 15 min) leads to their quantitative dehydrogenation to C_{60}. Anthracene and α-methylstyrene may serve as chemical dehydrogenating agents for the hydride $C_{60}H_{36}$ (the reduction of

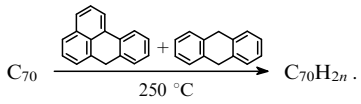
‡ $C_{60}H_2$: M^+, m/z 722; IR (KBr), ν/cm^{-1} = 2956, 1427, 1327, 1259, 1184, 1042, 791, 728, 725, 599, 590, 574, 565, 550, 527, 478; UV and visible spectra, λ/nm = 486, 457, 431, 404, 322, 308, 256, and 212.

§ SiO_2, CH_2Cl_2 : hexane = 1 : 3; $R_f(C_{60}H_{36}) = 0.37$[29,45] and $R_f(C_{60}H_{18}) = 0.15$.[45]

anthracene affords 1,2,3,4-tetrahydroanthracene, which is inert under these conditions).[45]

The conclusion about the structure of $C_{60}H_{36}$ obtained by the method described by Rüchardt *et al.*[45] was reached on the basis of the inability of the latter to be reduced to the corresponding radical-anion¶ on treatment with metallic potassium in dimethoxyethane. According to the authors,[45] this indicates the presence of isolated C=C bonds in the $C_{60}H_{36}$ molecule, as has been postulated for the product of the Birch reduction.

[7H]Benzanthrene plays the role of a catalyst in the hydrogenation of C_{60} and C_{70} by the method of Rüchardt *et al.*[45] using dihydroanthracene as the reducing agent (fullerene : catalyst : DHA = 1 : 5 : 100).[47]



The use of a catalyst made it possible to reduce the reaction temperature from 350 °C (for the noncatalytic reaction) to 250 °C, but the selectivity of the reaction became lower under these conditions. The C_{70} fullerene reacted more slowly than C_{60}. Deutero-derivatives of C_{60} and C_{70} have also been obtained by this method. The mass spectra of the reaction products formed in the presence of the catalyst are characterised by a wide mass distribution (Table 1). According to a mass-spectrometric study with ionisation of the sample by electron impact, in the case of C_{60} a hydride with a higher hydrogen content, namely $C_{60}H_{44}$, may be obtained under the conditions of the catalytic reaction. On the other hand, the mass spectra of the products of the reaction with ionisation of the sample by laser desorption (LD-MS) were identical with the spectra of the products obtained in the noncatalytic reaction, which indicates the same degree of reduction of C_{60} and C_{70} in both cases, namely to $C_{60}H_{36}$ and $C_{70}H_{36}$. This feature of the LD-MS method has also been noted by other researchers and has been explained by the possibility of the elimination of hydrogen from the unstable hydrides on laser desorption.

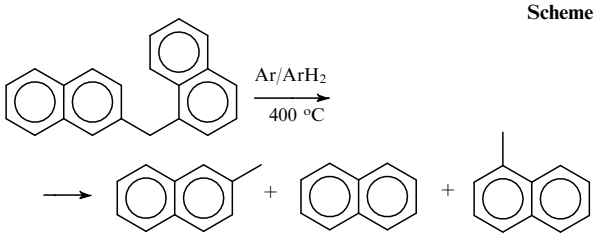
It is of interest that the main peak in the EI-MS of $C_{70}H_{36}$ (at m/z 876) indicates an increased stability of the hydride with 36 hydrogen atoms. The enthalpy of formation of $C_{70}H_{36}$ has been calculated: ΔH_f°(gas) = 490.2 kcal mol^{-1}.[47] Further reduction of C_{70} to $C_{70}H_{40}$ leads to an increase in ΔH_f°(gas) to 535.7 kcal mol^{-1}. Consequently the formation of $C_{70}H_{36}$ is the thermodynamically preferred process.

When C_{60} and mesitylene were refluxed (163 °C) under an inert atmosphere for 24 h, both the products of the dimerisation of mesitylene and the product of its addition to C_{60} were detected in the reaction mixture (C_{60} adducts with one, two, and three mesitylene residues), the yield of the products of the oligomerisation of mesitylene (dimers and trimers) exceeding by a factor of 7 the initial C_{60} concentration. One may therefore speak in this case of the catalytic activity of the C_{60} fullerene.[48]

The influence of C_{60} on the dehydrogenation of hydroaromatic compounds on heating has also been mentioned by Malhotra *et al.*[48] For example, in the dehydrogenation of 9,10-dihydrophenanthrene in the presence of C_{60}, the phenanthrene : dihydrophenanthrene ratio is 33, while in its absence, other conditions being equal, it is 1.3.[48] The C_{60} fullerene is then converted into reduced derivatives with different hydrogen contents. After prolonged heating, the hydrogenated fullerene derivatives are dehydrogenated, as in the case of $C_{60}H_{36}$.[45] Thus C_{60} behaves as a catalyst in this reaction.

The effect of C_{60} on the cleavage of the carbon–carbon bond in 1,2′-dinaphthylmethane has been investigated in the presence of hydrogen donors such as dihydroanthracene, dihydrophenanthrene, *etc.* (Scheme 4).[48] It was found that, when C_{60} is added to anthracene system, the rate constant of the reaction increases appreciably and the selectivity (the 2-methylnaphthalene : 1-methylnaphthalene ratio) changes. On hydrogenolysis of 1,2′-dinaphthylmethane in the absence of fullerene, the ratio is ~1.5, whilst in the presence of fullerene-containing systems it reaches ~4.4–5.4. The results indicate the involvement of C_{60} in the acceptance of hydrogen atoms from the hydroaromatic compounds or the corresponding hydroaryl radicals and in the subsequent hydrogen transfer to 1,2′-dinaphthylmethane.

Scheme 4



Ar/ArH_2 = anthracene/9,10-dihydroanthracene, pyrene/4,5-dihydropyrene, or phenanthrene/9,10-dihydrophenanthrene.

The hydroalkylation of fullerene by unsaturated compounds, such as hept-1-ene and 4-allylanisole, with formation of fullerene alkyl hydrides, has been reported.[49]

It has been observed that, when various hydrocarbons, including alkanes, are come into contact with fullerenes (fullerene cocoons)† at high temperatures (500–700 °C), large amounts of molecular hydrogen and of the products of the dehydrogenation of the hydrocarbons are evolved into the gas phase.[50] The reactions were carried out at a very low pressure of the hydrocarbons (1 Torr),[50] which indicates a high activity of fullerenes in the activation of C–H bonds, including the bonds in alkanes. In contrast to industrial pyrolytic processes, lower olefins predominate in the reaction products in this instance. For example, ethene, propene, and hydrogen have been obtained from hexane in the complete absence of ethane, propane, and C_4 hydrocarbons.[50] Thus, apart from the dissociation of the C–H bonds, the cracking of strong C–C bonds in alkanes also takes place effectively on the fullerene cocoons. The pyrolysis of toluene is also accompanied by the dissociation of the $CH_3-C_6H_5$ bond, which is indicated by the presence of methane and benzene in the reaction products.[50]

The activation of methane also becomes possible in the above temperature range (the C–H bond energy is 105 kcal mol^{-1}).[51–53] The threshold temperature of the onset of pyrolysis of methane on fullerene black‡ as the catalyst is 600 °C, which is lower by 250 °C than the reaction threshold in the absence of a catalyst and lower by 100–200 °C than the threshold temperatures for graphite, activ-ated charcoal, and other carbon catalysts.[51–53] High degrees of con-version, of methane (dozens of %) are attained under the conditions of a flow reactor at temperatures above 900 °C. The dehydrogenating activity of the initial fullerene black is then so high that at the beginning of the reaction hydrogen is virtually the only gaseous product.[53] Only after the accumulation of a certain amount of pyrolytic carbon and the concomitant decrease in the dehydrogenating activity of the catalytic system do gaseous hydrocarbons, among which ethene predominates, appear in the products. Further accumulation of pyrolytic carbon leads to a decrease in both the degree of conversion of methane and in the selectivity with respect to ethene.[53] This undesirable phenomenon was overcome by diluting the initial stream of methane with hydrogen.[53]

¶ All attempts to observe the EPR spectrum of the radical-anions of the hydrogenated and deuterated fullerenes were unsuccessful.[45]

† Fullerene cocoons are polymeric structures, which are nonsublimable (in contrast to fullerenes) at high temperatures and in which the fullerene molecules are linked to one another by oxygen bridges, the number of which is approximately equal to the number of fullerene molecules.[50]

‡ Fullerene black is the finely dispersed carbon material remaining after the extraction of fullerenes with a suitable solvent from the fullerene-containing soot obtained on electric arc vaporisation of graphite under an inert gas atmosphere.

It has been observed[53] that the addition of hydrogen to methane can alter drastically the process selectivity. At a sufficiently high dilution, the reaction begins immediately, without the induction period mentioned above, whereupon virtually pure ethene is formed (the selectivity with respect to ethene is 90%–94%) while the amount of propene does not exceed 6%–10% and there are only traces of other products.[53] The degree of conversion of methane is comparatively low (~4%), but remains stable for many hours at 1000 °C. The accumulation of pyrolytic carbon is not observed under these conditions.

Such influence of dilution on the process is fully reversible, which suggests that the mechanism of this interesting phenomenon involves the dynamic blocking by hydrogen of the most active dehydrogenation centres on the surface of fullerene black. Fullerene black consists mainly of three–five layer stacks of markedly curved graphene sheets with a local radius of curvature of the order of the dimensions of the usual fullerenes.[54] The curvature caused by the presence of five- and seven-membered rings in the structure of the sheet arises under the highly non-equilibrium conditions in the electric arc, characterised by high temperature and carbon species concentration gradients. This distinguishes fullerene black from all industrial blacks, activated charcoals, and graphite, the only basic structural element of which is absolutely planar graphene sheets, *i.e.* planar two-dimensional macromolecules consisting of carbon atoms, forming adjacent hexagons. The curvature of the carbon surface in fullerenes and in fullerene black may be the cause of their higher reactivity towards dihydrogen and C–H bonds.

The mechanism of the activation of hydrocarbons RH in the presence of fullerenes is as follows. The C–H bond is activated by the strained $C^*{=}C^*$ double bond of the curved carbon surface in the primary step of the interaction of the hydrocarbon with fullerene, which results in the formation of the $R-C^*-C^*-H$ fragment. The subsequent migration of hydrogen atoms and the radicals R on the surface, multiple reversible addition of the RH molecules and hydrogen, reactions of the two-centre and β-elimination types, and also the dissociation of the free radicals R and other processes possible at sufficiently high temperatures are responsible for the formation of the set of products in the liquid-phase and gas-phase reactions investigated. Thus methylated derivatives of fullerenes, namely $C_{60}(CH_3)_n$, were detected in the mass-spectrometric analysis of the fullerene-containing soot, carried out after the high-temperature dehydrogenation of methane.[51] Modification of the catalyst, for example doping of the fullerene-containing soot with potassium, increases the selectivity in the formation of higher hydrocarbons from methane.[52]

4. Reduction of fullerenes in a metal–acid system

The reduction of C_{60} in metal (M)–acid systems, where M = Sn[$E^{Ox/Red}(Sn^{2+}/Sn) = -0.75$ V], Fe[$E^{Ox/Red}(Fe^{2+}/Fe) = -1.05$ V], and Zn[$E^{Ox/Red}(Zn^{2+}/Zn) = -1.37$ V], has been investigated. The potentials were measured relative to Fc^+/Fc (Fc = ferrocene).[55] In principle, these results make it possible to obtain the anions C_{60}^- and C_{60}^{2-} since the potentials for C_{60}^0/C_{60}^- and C_{60}^-/C_{60}^{2-} are −0.98 and −1.37 V relative to Fc^+/Fc. However, the Sn–acid and Fe–acid systems proved to be ineffective for the reduction of C_{60} and only the Zn–acid system was found to be suitable for such purposes. The acids employed are 6 M or 12 M HCl, glacial CH_3COOH, and concentrated H_2SO_4. When a toluene solution of C_{60} is refluxed under an inert atmosphere, a mixture consisting of 7% of $C_{60}H_2$, 3% of $C_{60}H_4$, and 1% of $C_{60}H_6$ is formed. It was separated by means of HPLC. It contains also small amounts of fullerenes with a higher hydrogen content ($C_{60}H_6$–$C_{60}H_{22}$), but these were not isolated.[55] The mass spectra of the fullerene hydrides obtained by this method demonstrate a strong tendency of the products for fragmentation back to the parent C_{60} on ionisation. It has been demonstrated that the substance with a mass of 722, present in the reaction mixture in the largest amount, has the same spectroscopic and chromatographic characteristics as 1,2-$C_{60}H_2$.[33] Thus, under the conditions indicated, mainly the most stable dihydrofullerene isomer (1,2-$C_{60}H_2$) is formed in the C_{60}–Zn–acid system. Treatment of the reaction mixture obtained as a result of the interaction of C_{60} with zinc in hydrochloric acid with DDQ leads to C_{60}, which confirms the formation of hydrogenated C_{60} derivatives.

The reduction of C_{60} and C_{70} in the Zn–conc. HCl–toluene (benzene) system under an inert atmosphere takes place rapidly even at room temperature and leads to the preferential formation of $C_{60}H_{36}$, $C_{70}H_{36}$, and $C_{70}H_{38}$ in the absence of light.[56] In the case of C_{60}, appreciable amounts of more highly hydrogenated derivatives are also formed in this case: $C_{60}H_{38}$ (15%) and $C_{60}H_{40}$ (3%).[56] The C_{70} fullerene is reduced at a lower rate than C_{60}. Furthermore, the compound $C_{70}H_{36}$ is thermally less stable than $C_{60}H_{36}$.

The sensitivity of fullerene hydrides synthesised by this method to oxygen increases appreciably in solution in the presence of light. The peaks due to the initial fullerenes and their lower hydrides are therefore absent from the mass spectra of $C_{60}H_{36}$, $C_{70}H_{36}$, and $C_{70}H_{38}$, obtained with the aid of ionisation by electron impact, only in the case where the spectra have been run immediately after work up. Otherwise, peaks corresponding to completely dehydrogenated products (C_{60} and C_{70}) and the lower hydrides ($C_{60}H_{18}$ in the case of $C_{60}H_{36}$), as well as fullerols appear in the mass spectra. The formation of highly hydrogenated fullerenes, including $C_{60}D_{44}$ and $C_{70}D_{48}$ on treatment with Zn in concentrated DCl, is associated with the greater stability of the C–D bonds compared with the C–H bonds, as a result of which the loss of the resonance energy of the initial fullerene is partly compensated. The hydrogen atoms in fullerene hydrides do not undergo H/D exchange in the absence of light either with D_2O, or with $D_2O/NaHCO_3$, or with $D_2O/NaOH$, which indicates a decrease in the acidity of the C–H bond in $C_{60}H_{36}$ compared with, for example, the acidity of this bond in the adduct of C_{60} with morpholine [$NH(CH_2)_4O$] having the composition $HC_{60}N(CH_2)_4O$ since in the latter case hydrogen rapidly exchanges with CH_3OD.[5, 57]

The hydrides $C_{60}H_{36}$ and $C_{70}H_{36}$ are resistant to further reduction by hydrogen in the presence of the Rh/Al_2O_3 catalyst (toluene is used as the solvent), but they tend to form trimethylene adducts (this is indicated by the appearance in the mass spectrum of peaks with m/z 798, 840, and 882 in the case of $C_{60}H_{36}$) via an unknown mechanism.[56] When the reaction was carried out in benzene-d_6 (as a solvent), H/D exchange between the fullerene hydride and the deuterium of the solvent was observed.[56]

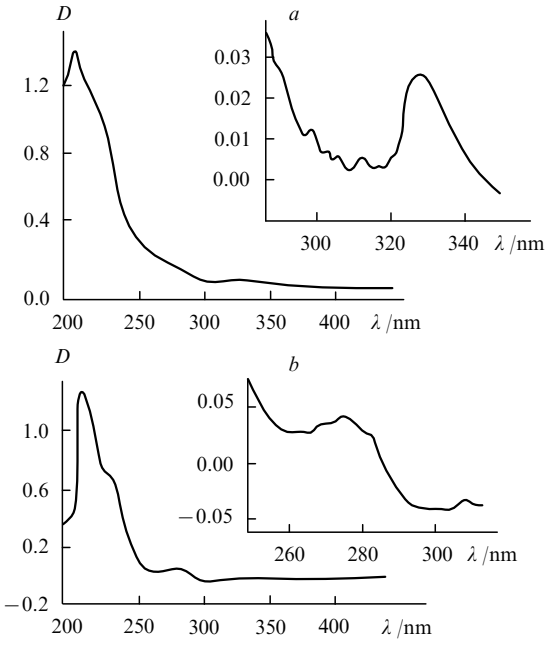


Figure 3. Absorption spectra of $C_{60}H_{36}$ (*a*) and $C_{70}H_{36}$ (*b*) (higher hydrides are present as impurities).[56]

The UV spectrum of $C_{70}H_{36}$ has a broad band with a maximum at 275 nm and a shoulder at 223.5 nm (Fig. 3), which are close to the wavelengths λ for naphthalene (221 and 258–280 nm).[56] According to the authors,[56] this is consistent with the aromatic structure proposed for $C_{70}H_{36}$.[58]

5. Reduction of fullerenes by hydrogen

The direct reduction of C_{60} and C_{70} has been carried out in the solid phase at a hydrogen pressure of 50–80 MPa and a temperature of 573–623 K without using a catalyst.[59] Fullerene hydrides having the composition $C_{60}H_x$ ($x = 2-18$) and $C_{70}H_y$ ($y = 4-30$), identified with the aid of mass spectrometry, are then formed. The authors [59] also attempted to answer the question whether hydrogen atoms or molecules can be added at a high pressure and an elevated temperature to endohedral positions in the fullerene molecule. In order to avoid losses of fullerene, the reaction was carried out in a sealed capsule. The material of the capsule (25% Ag–75% Pd alloy, Au, or glass), in which the hydrogenation is carried out, does not affect the yield of the products and the rate of hydrogenation. This provided grounds for the assumption that the hydrogenation proceeds only under the influence of hydrogen and is initiated by small amounts of atomic hydrogen, which is generated in the reaction medium at these temperatures and pressures.

Heating of the C_{60} fullerene in a sealed AgPd capsule in a H_2 atmosphere at a temperature $\geqslant 950$ K leads to the complete disappearance of the specimen. Since neither C_{60} nor its hydrides can diffuse from the capsule, under the given experimental conditions fullerene apparently decomposes to low-molecular-mass fragments, which react with the material of the capsule and the presence of hydrogen then plays an important role.

The study of the products of the direct hydrogenation of fullerene showed that hydrogen usually if not always adds exohedrally to the fullerene skeleton. In order to demonstrate this fact, use was made of the proton transfer reaction

$$Py + C_{60}H_x^+ \longrightarrow PyH^+ + C_{60}H_{x-1}\,.$$

Pyridine (Py, proton affinity 220.4 kcal mol^{-1}) is a stronger base than C_{60} (proton affinity 205 kcal mol^{-1}), so that the interaction can occur only when all or some of the hydrogen atoms in the fullerene hydride are bound exohedrally, although the possibility of the endohedral binding of hydrogen is also not ruled out. Hydrogenation lowers somewhat the ionisation potential of fullerene: $I(C_{60}H_x = 2-18) \leqslant 7.53$ eV, while $I(C_{60}) = 7.6$ eV. It has been noted that the hydride $C_{60}H_x$, obtained by direct solid-phase hydrogenation is distinguished by a greater stability than the specimens obtained by other methods.[29,60]

Fullerite§ (a mixture of C_{60} and C_{70}) was hydrogenated (~ 1 h) by hydrogen at 400 °C and a H_2 pressure of 6.9 MPa using ethyl iodide as the promoter of the formation of atomic hydrogen in the system.[61] In the absence of C_2H_5I, hydrogenation does not occur. An increase in temperature and pressure leads to a decrease in the degree of hydrogenation. Mass-spectrometric analysis of the reduced fullerite by FAB-MS technique showed that a mixture of hydrides $C_{60}H_{36}$ and $C_{70}H_{36}$ is mainly formed in the reaction. The use of 'harder' mass-spectrometric methods, such as EI and LD, proved impossible owing to the thermal decomposition of the product to compounds with lower molecular masses ($C_{60}H_{18}$, $C_{60}H_8$, *etc.* in the case of $C_{60}H_{36}$). No spectroscopic evidence for the ethylation or iodination of fullerene under these conditions was found. The reaction product is insoluble in the majority of organic solvents and is only slightly soluble in nitrobenzene, which distinguishes it from the hydride obtained by Birch reduction [29] or by the transfer hydrogenation.[45]

$$C_{60} \xrightarrow[450\ ^\circ C,\ 70\ atm]{C_2H_5I,\ H_2} C_{60}H_{2n}\,.$$

§ The solid crystalline material consisting of pure fullerenes or their mixtures is called fullerite.

The solid-phase ^{13}C NMR spectrum of polyhydrogenated fullerene $C_{60}H_{36}$, obtained by radical hydrogenation, indicates the presence of a single highly symmetrical compound, possibly of D_{3d} or C_{3i} symmetry.[61] On the other hand, Buhl *et al.*[62] see no agreement between the experimental ^{13}C NMR spectrum of $C_{60}H_{36}$ [61] and the D_{3d} structure.

The reaction of C_{60} (up to 90% in the mixture) with an ultrasonic molecular beam of H_2 or D_2 has been investigated at 540–750 °C and a pressure of 100–500 Torr.[63] It was found that the interaction of H_2 with C_{60} under these conditions leads to both the hydrogenation of fullerene (up to eight hydrogen atoms may add to C_{60}) and to the formation of low-molecular-mass hydrocarbon species as a consequence of the disruption of the C_{60} skeleton. When H_2 is replaced by D_2, a large isotope effect is observed. The main product is $C_{60}H_2$, the yield of which depends both on the H_2 pressure and on the temperature.

$$C_{60} + H_2(g) \longrightarrow C_{60}H(g) + H(g),$$
$$H(g) + C_{60}(g) \longrightarrow C_{60}H(g),$$
$$C_{60}H(g) + H_2(g) \longrightarrow C_{60}H_2(g) + H(g),$$
$$2C_{60}H(g) \longrightarrow C_{60}H_2(g) + C_{60}(g).$$

Solid C_{60} has been hydrogenated by atomic hydrogen at 77 K (in a cyclohexane matrax).[64] The $C_{60}H$ ($g = 2.00218 \pm 0.0004$), $C_{60}H_{2n+1}$, and $C_{60}H_{2n}$ species were identified by EPR and IR spectroscopy and FAB-MS technique.

The hydrogenation of thin C_{60} films by atomic hydrogen has been investigated with the aid of the plasma desorption method.[65] The approach proposed [65] makes it possible to determine the degree of hydrogenation of C_{60} molecules. It was found that hydrogen is bound covalently to the fullerene molecule with formation of the hydride $C_{60}H_n$ ($n = 2-24$). The authors rule out the possibility of the formation of fullerene hydrides by the interaction of C_{60} with the residual toluene in the film under the conditions of the mass-spectrometric analysis.

An attempt to implant a hydrogen atom inside the C_{60} molecule has been reported [plasma, 10–25 eV, 550–600 °C, $(5-10) \times 10^{-4}$ Torr]. It has been shown with the aid of HPLC, ^1H NMR, and mass spectrometry that hydrogen adds exohedrally with formation of the compounds $C_{60}H_2$ and $C_{60}H_4$. No evidence has been obtained for the formation of complexes with endohedrally bound hydrogen under these conditions.[66]

We may note that the addition of a H atom to C_{60}^+ in the gas phase takes place very effectively, the bimolecular reaction rate constant being $k \approx 6 \times 10^{13}$ cm^3 mol^{-1} s^{-1} at 294 K and a helium pressure of 0.4 Torr.[67] Under the same conditions, the reaction of C_{60}^+ with molecular hydrogen does not occur,[68] but a C_{60} ion accelerated up to an energy of 5–6 keV is apparently capable of incorporating a H_2 molecule into the carbon framework with formation of the endohedral complex $H_2@C_{60}^+$.[69]

The hydrogenation of the molecules of fullerenes and other neutral C_n carbon clusters in the gas phase at a high temperature has been investigated by the TOF-MS technique with LD evaporation of the test substance for the wide range $n = 6-75$.[70] The clusters were obtained by the laser pulse evaporation of graphite and were mixed with D_2 in a flow reactor. The kinetics of the variation of the C_n concentrations and of the formation of the C_nD_m products ($m = 1-4$) have been investigated. Deuterated clusters are formed as a result of the successive addition of D atoms via the reaction involving direct abstraction from the D_2 molecule ($k \approx 10^{11}$ cm^3 mol^{-1} s^{-1} at 2800 K).

$$C_n + D_2 \longrightarrow C_nD + D.$$

In certain cases, excited C_nD^* species undergo unimolecular decomposition with the preferential formation of the compound C_3($p = 3$):

$$C_nD^* \longrightarrow C_{n-p}D + C_p\,.$$

In the case of 'even' C_{2n} clusters with $n < 20$, the reaction product $C_{2n}D_2$ is a linear polyyne (a carbyne), which is inert in relation to more extensive hydrogenation. An attempt may be

made to use this fact in order to obtain the crystalline form of the carbyne by depositing on a cold support the products of the reaction of graphite vaporised in a hydrogen atmosphere. The possibility of the existence of such a form of the carbyne stable at room temperature is indicated by experiments on the condensation of the products of the electric spark disintegration of graphite on a copper plate under an argon atmosphere (0.5 Torr)[71] and also by the presence of linear carbon molecules in the fullerene black obtained by the electric arc [72] or laser [73] vaporisation of graphite.

The 'odd' C_{2n+1} clusters react with D_2 at a higher rate than the 'even' clusters.[70] This difference increases progressively with increase in n in the fullerene mass range ($n > 36$), where the reactivity of even clusters (fullerenes) diminishes and that of the odd clusters (structures with open carbon shells of a radical character with a larger geometrical collision cross-section) increases.[70]

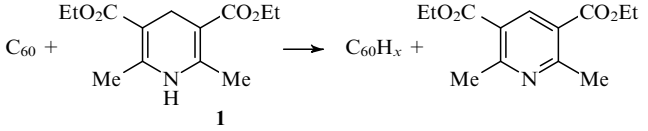
The high-temperature hydrogenation reactions of fullerenes and their precursors influence the yield of fullerenes in hydrocarbon flames and in a carbon arc. Even several per cent of hydrogen in helium fully blocks the formation of C_{60} in the electric arc vaporisation of graphite.[74] The possibility of the formation of the hydrides $C_{60}H_x$ in this process for a low hydrogen content in the gaseous medium has not been specially investigated. On the other hand, under a hydrogen atmosphere, open carbon nanotubes appear in the cathodic deposit formed in a d.c. carbon arc.[75, 76] Under these conditions, the inner channel of the open nanotubes is free of the amorphous carbon deposits characteristic of tubes opened by treatment with strong oxidants. In addition, the number of spherical carbon nanoparticles in the deposit decreases sharply under a hydrogen atmosphere.[75–77] Thus the use of hydrogen is extremely promising for the solution of the problem of the preparation of open and pure nanotubes. The effect of hydrogen consists in this instance of the hydrogenation of the end-face of the growing open nanotube with formation of relatively stable C–H bonds, which prevent the formation of five-membered rings and hence the closure of the tube when the temperature is reduced.[75, 76]

6. Reduction of fullerenes by organic compounds under irradiation

In the study by the EPR method of the products formed in the photolysis (high-pressure Hg/Xe lamp) of a benzene solution of C_{60} containing thiophenol, cyclohexa-1,4-diene, or Bu_3SnH, it was found that the EPR spectrum consists of two lines with a splitting of 33 G.[78] The authors assigned this spectrum to the radical $C_{60}H^{\bullet}$ — the initial product of the reaction of the photogenerated hydrogen atom with C_{60} (the hydrogen atoms are formed on photolysis of thiols, tin hydrides, and cyclohexa-1,4-diene).

On heating (100 °C, toluene) or flash photolysis (Nd^{3+} : YAG-laser, $\lambda = 532$ nm, benzonitrile) of the C_{60} fullerene–diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1**) reaction mixture, appreciable changes are observed in the absorption spectrum of C_{60} in the visible region: bands at 434 and 708 nm, characteristic of dihydrofullerene, appear in it, while the bands characteristic of free C_{60} vanish. It has been shown by ^{1}H NMR that the solution contains the diethyl ester of 2,6-dimethylpyridine-3,5-dicarboxylic acid — the product of the dehydrogenation of compound **1**. The formation of the hydrides $C_{60}H_x$ ($x = 2, 4, 6$) has been demonstrated mass-spectrometrically.[79]

Scheme 5



1

7. Catalytic hydrogenation of fullerenes

The possibility of the catalytic hydrogenation of C_{60} in the presence of transition metals has been investigated.[80–85] It was found that, in the presence of Ru/C, Pt/C, and Pd/C, fullerene is hydrogenated (H_2 pressure 100 atm, 180 °C), affording a low yield of $C_{60}H_{36}$ (a mixture of $C_{60}H_{36}$ and $C_{60}H_{18}$ is formed depending on the hydrogen pressure). The activity of the catalysts varies in the sequence Pt < Ni < Pd < Ru. The low yield of the hydrogenated products is due to a number of causes, including the high adsorption capacity of the activated charcoal, which leads to losses of fullerene and its hydrides,and also to the hydrogenation of the solvent (toluene) on certain catalysts (Ru/C, Ni/diatomite). The formation of C_{60} complexes with palladium, stable up to 120 °C (their dissociation begins above this temperature), has been reported.[86] This is in fact the temperature of the onset of the hydrogenation of C_{60} in the presence of Pd/C.[80, 81] The fullerene hydrides formed are unstable even under an inert atmosphere.

The hydrogenation of C_{60} has been investigated in C_6D_6 in the presence of Rh/Al_2O_3.[87] Comparison of the ^{1}H and ^{13}C NMR spectra of the product and of $C_{60}H_2$ synthesised by the method described by Henderson and Cahill [33] demonstrated their complete identity. It was found that the yield of $C_{60}H_2$ in the hydrogenation of C_{60} in the presence of Rh/Al_2O_3 initially rose, reaching ~14%, and then diminished, the yield of the more highly hydrogenated fullerenes increasing under these conditions (HPLC data). The reaction product was fairly stable in the reaction medium, but it decomposed in the light on treatment with O_2 and was partly converted into C_{60}.

The reactivity of the coordinated C_{60} fullerene has been demonstrated in relation to the hydrogenation in the solid phase of the palladium fulleride $C_{60}Pd_{4.9}$ by molecular deuterium (473–673 K, D_2 pressure 20 atm).[88] In the course of the reaction under relatively mild conditions, a set of deuterofullerenes $C_{60}D_x$ ($x = 2–26$) are formed, the main products being those with $x = 2$, 4, 18, and 26. Deuterofullerenes containing an odd number of deuterium atoms have also been detected by means of field desorption (FD-MS) mass spectrometry. The IR spectrum of the fullerene deuteride obtained at 473 K contains a broad band with the centre at 2150 cm^{-1} [ν(C–D)], the intensity of which increases with increase in the reaction temperature. The spectrum of a solution of the fullerene deuteration product in the visible range contains bands at 407(C_{60}), 435, and 715 nm.

The direct solid-phase synthesis of $C_{60}H_2$ from C_{60} and the stoichiometrically controlled amount of hydrogen has been achieved (reaction temperature 400–500 °C, reaction time 12 h).[89] Palladium hydride was used as the source of activated hydrogen. The main product is 1,2-$C_{60}H_2$ (~15%). $C_{60}H_4$ is also formed in a small amount (3%–5%) in the form of the thermodynamically most stable 1,2,3,4-$C_{60}H_4$. The isomerisation of the fullerene hydrides $C_{70}H_2$ and $C_{60}H_4$ to the most stable 1,2- and 1,2,3,4-isomers had already been observed.[42, 43] With increase in the hydrogen pressure, the yield of $C_{60}H_4$ rises, while the amount of dihydrofullerene remains unchanged.

The catalytic hydrogenation of C_{60} in boiling toluene in the presence of Ru/C leads to highly hydrogenated compounds (up to $C_{60}H_{50}$).[83] The degree of hydrogenation increases with increase in the hydrogen pressure and reaction temperature. The signal, corresponding to the ion with m/z 780, which belongs according to the authors,[83] to the hydride $C_{60}H_{60}$, has been detected in the mass spectrum (FD-MS) of the C_{60} hydrogenation products obtained at 280 °C and a H_2 pressure of ~130 atm.

In boiling toluene, the fullerene hydrides $C_{60}H_{18}$, $C_{60}H_{36}$, $C_{60}H_{40}$ are dehydrogenated by DDQ, the yields of C_{60} being 51%, 48%, and 45% respectively.[82] The hydrogenation of C_{70} under similar conditions (Ru/C catalyst) leads to $C_{70}H_{36}$.[84] The dehydrogenation of the latter with the aid of DDQ also proceeds almost quantitatively.

$$C_{60}(C_{70}) \xrightarrow[110\ ^{o}C,\ C_6H_5CH_3]{H_2,\ Ru/C} C_{60}H_{2n}(C_{70}H_{2n}).$$

The dehydrogenation of the hydrofullerenes $C_{60}H_{2n}$ and $C_{70}H_{2n}$ on treatment with DDQ in the presence of catalysts (Ru/C) or on heating has also been investigated.[85] High yields of fullerenes are obtained only in the presence of DDQ as the dehydrogenating

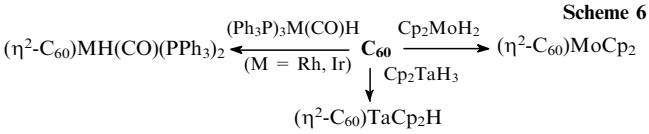
agent, whereas refluxing of $C_{60}H_{36}$ in toluene in the presence of Ru/C leads to the appearance of only 1% of C_{60} (FD-MS).

It has been found that the temperatures corresponding to the loss of 1% of mass for $C_{60}H_{18}$ and $C_{60}H_{36}$ are 164 and 175 °C (in a nitrogen atmosphere) and 348 and 247 °C (in air) respectively. The degrees of conversion of $C_{60}H_{18}$ and $C_{60}H_{36}$ in nitrogen at 600 °C are 30.5% and 26.8%, whereas at 400 °C in air the corresponding values are 56.6% and 40.1%.[85]

8. Interaction of fullerenes with transition metal hydride complexes

Treatment of solutions of C_{60} (C_{70}) in toluene, benzene, or CH_2Cl_2 with metal (Ir, Rh, *etc.*) hydride complexes at room temperature leads to an instantaneous change of the colour of the solution. Three bands then appear in the electronic spectra of the solutions at λ = 435, 604(600), and 640(630) nm. Their intensity is significantly higher than the intensity of the absorption of fullerenes in this region, which indicates the quantitative formation of metal complexes with fullerene (Scheme 6). The latter were characterised by a spectroscopic method.[90–93] The molecular and crystal structures of the complex η^2-$C_{60}Rh(CO)H(PPh_3)_2$ have been determined.[93] The composition of the complexes (η^2-C_n)IrH.(CO)$(PPh_3)_2$ (n = 60, 70), their configuration, and the position in the fullerene nucleus of the C=C double bond coordinated to the metal were established from the IR spectra (by comparative analysis relative to the spectra of the corresponding deuterated analogues) and ^1H and ^{31}P NMR spectroscopic data.[91]

Scheme 6



The complexes (η^2-C_{60})$TaCp_2H$ and (η^2-C_{60})$MoCp_2$ are formed on interaction of the hydride complexes Cp_2TaH_3 and Cp_2MoH_2 with fullerene. Molecular hydrogen is apparently evolved as a result of the reaction, but its presence in the gas phase has not been demonstrated.[90] The interaction of the 16-electron square planar complex $PtHCl(PPh_3)_2$ and of the 18-electron octahedral complex $Ir(H)_2Cl(CO)(PPh_3)_2$ with the C_{60} fullerene on refluxing an alkaline (NaOH) solution of the reactants in a 1 : 2 ethanol–benzene mixture leads to the formation of (η^2-C_{60})$Pt(PPh_3)_2$ and (η^2-C_{60})$IrH(CO)(PPh_3)_2$ respectively.[94]

9. Hydrogenation of mechanical mixtures of powdered fullerite and hydrogen-sorbing metals and intermetallic compounds

The study of the hydrogenation and dehydrogenation reactions of fullerenes is of interest both from the standpoint of the development of systems for the accumulation and storage of hydrogen and from the standpoint of other practical applications.[3, 28, 95, 96] Such systems are constructed nowadays on the basis of intermetallic compounds or metals capable of absorbing considerable amounts of hydrogen selectively and reversibly.[97] In this respect, fullerene hydrides which have a low density and are capable of containing up to 8 mass% of hydrogen (as in the $C_{60}H_{60}$ hydride), are of special interest. However, direct noncatalytic hydrogenation of the C_{60} fullerene proceeds effectively only at high pressures (50–85 MPa) and temperatures (573–623 K).[59] The other methods of synthesis of fullerene hydrides listed above considered as systems for the reversible storage of hydrogen have also proved to be relatively unattractive owing to the difficulty of achieving multiple repetition of the 'hydrogenation–dehydrogenation' cycle in the presence of solvents in the system. This difficulty can be overcome by developing processes for the solid-phase catalytic hydrogenation of fullerenes. The choice of hydrogen-sorbing intermetallic compounds and metals as potential catalysts of such processes is natural because hydrogen possesses a high chemical reactivity at the instant of its evolution from metal hydrides.[98]

The reactions involving the hydrogenation of fullerenes by molecular hydrogen in the solid phase in the presence of intermetallic compounds and metals effectively sorbing hydrogen have been achieved in relation to the compounds $LaNi_5$, $LaNi_{4.65}Mn_{0.35}$, $CeCo_3$, metallic palladium and vanadium, and also the hydrides of the above compounds.[99–101] The use of hydrides as the initial components of mechanical mixtures with fullerenes is preferable, because, owing to the high brittleness of the hydrides, the preparation of smaller particles is ensured when mixtures are treated in a vibromill compared with powdered metals and intermetallic compounds. When hydrides are used, it is possible to avoid the undesirable oxidation of the surface of the particles in the course of the mechanical milling of their mixture with fullerite powder (such milling is necessary to ensure the homogeneity of the mixture and to increase the surface of contact of the two initial components).[99–101]

The hydrogenation of fullerenes in such mechanical mixtures proceeds quite effectively already at a hydrogen pressure of 1–2.5 MPa and temperatures in the range 573–673 K, which is indicated, for example, by the appearance in the IR spectra of the product (after the treatment of the mixtures with deuterium under these conditions)[99–103] of an intense absorption band at 2120 cm^{-1} (stretching vibrations of the C–D bonds).[88] According to the results of chemical analysis, the deuterium content in the mixture specimens increases monotonically with increase in the deuteration temperature to 673 K, with increase in the D_2 pressure, and with increase in the number of 'D_2 sorption-desorption' cycles. The product with the highest deuterium content (24–26 deuterium atoms per C_{60} fullerene molecule) has been obtained in the interaction of D_2 with mixtures of fullerite and intermetallic compounds or metals at a gas pressure of 2.5 MPa and for a sevenfold repetition of the 'heating to 673 K (1 h)–cooling to 293 K (1 h)' cycle.[99–101] Hydrides of similar composition are formed also when the usual hydrogen is employed.

It has been found with the aid of differential thermal analysis (DTA) and thermogravimetry of the hydrogenated mechanical mixtures that the endothermic decomposition of the fullerene hydride takes place in all cases at 800 K with evolution of 1 mass % – 3 mass % of gaseous hydrogen. The constancy of the decomposition temperature (800 K) means that the presence of metals and intermetallic compounds does not affect the dehydrogenation of fullerene hydrides, in contrast to the hydrogenation process, which is appreciably facilitated in the presence of these mechanical mixtures (a decrease in hydrogen pressure from 50–80 to 1–2.5 MPa). This may be induced by the irreversible transfer of activated hydrogen from the metal to the C=C bonds of the fullerene component of the mixture. It is known that the effective action of the composite system requires, apart from fine mechanical milling of the mixture in a vibromill ensuring a high area contact of the components, also several 'hydrogenation–dehydrogenation' cycles, during which the molecular structure of the contact apparently changes with removal of surface oxygen and the probable formation of M–C bonds. The irreversible hydrogen transfer from the metal to the C–C bond apparently actually occurs with participation of M–C bridges. At 800 K fullerenes are effectively dehydrogenated, the M–C bonds are to a large extent dissociated, preventing the reverse hydrogen transfer to the metal, whereupon the organic subsystem must evolve the excess hydrogen spontaneously without the participation of the metals.

The hydrogenated specimens of the mechanical mixtures contain, apart from fullerene hydrides, also the hydride phases of the corresponding intermetallic compounds or metals,[99–101] which is indicated by clearly distinguishable endothermic effects in the range 350–600 K. The decomposition of the corresponding hydrides of palladium (360 K)[99] and vanadium (450 and 550 K) and of the hydride phases of the intermetallic compounds $LaNi_{4.65}Mn_{0.35}H_x$ and $CeCo_3H$ (500–600 K), accompanied by the evolution of hydrogen, takes place at these temperatures.[100, 101] The amount of evolved hydrogen is correlated with the content of the metal or the intermetallic compound in the

composite mixture and is usually 70% – 90% of the amount of hydrogen in the fully saturated stoichiometric hydrides.

Intense exothermic peaks unaccompanied by a change in the mass of the specimen have been observed on the DTA curves in the temperature range 950 – 1000 K for all the hydrogenated compositions (except the palladium ones) investigated.[99–101] Their appearance is associated with the irreversible chemical interaction of fullerenes with intermetallic compounds or metals, leading to the formation of metal carbides. In the hydrogenation in the presence of vanadium, the endothermic effect observed at 900 K is due to the decomposition of fullerenes and the formation of the vanadium carbide $VC_{0.8}$ with a NaCl type lattice.[101] In the case of compositions based on fullerite and the intermetallic compounds $LaNi_5$, $LaNi_{4.65}Mn_{0.35}$, and $CeCo_3$, the products of the high-temperature heating of the hydrogenated specimens are the hydrides of the lanthanide and the metallic phases of the corresponding transition metal.[100]

In the case of palladium, the high-temperature exothermic effect is not observed and the initial phase state of the metal does not change.[99] Bands characteristic of fullerenes are retained in the IR spectra of specimens of the mixed palladium compositions heated to 1200 K, in contrast to the compositions based on vanadium, for which analogous heat treatment leads to the complete disappearance of the fullerene bands. The palladium compositions partly dissolve in toluene, in contrast to the insoluble vanadium compositions.

The absorption bands due to fullerenes are absent from the IR spectra of specimens based on intermetallic compounds heated to 1200 K, while peaks due to the metallic nickel, manganese, or cobalt phase respectively can be seen on the X-ray diffractograms. Magnetic measurements have shown that the content of ferromagnetic nickel and cobalt particles in the products of the heat treatment at 1200 K is approximately equal to the amount of Ni and Co in the initial intermetallic compounds,which indicates the almost complete decomposition of the latter. This finding and the decomposition of the fullerenes mentioned above suggest that the lanthanide metal remains in the specimen in the form of the X-ray-amorphous carbide. The chemical interaction of intermetallic compounds and fullerenes proceeds after the completion of the decomposition of the fullerene hydrides, which apparently facilitates the formation of carbides as a result of the removal of the impurity oxygen (there is also a possibility of the preliminary formation of a small number of metal – carbon bonds).

Thus the presence of carbide-forming metals (including those in the intermetallic compounds) in the compositions leads to the degradation of the fullerene structures even when the temperature corresponding to the complete evolution of hydrogen from the hydrogenated composites (800 K) is only slightly exceeded. The formation of metal carbides and metallic phases observed under these conditions lowers the capacity of the composites with respect to hydrogen and the sorption – desorption reversibility. The elimination of this effect, which is undesirable for hydrogen storage systems, may involve the determination of the upper permissible limiting temperature to which the composite material may be heated and also the search for materials for which the formation of carbides is difficult or impossible.[101]

One of the most significant obstacles on the way to the technical realisation of fullerene-based hydrogen accumulators is the evolution of a large amount of heat in the adsorption of hydrogen by compacted fullerite,[28] which,when combined with the low thermal conductivity of the latter, leads to its mechanical disintegration and also to the retardation of the saturation by hydrogen and failure of the latter to reach completion. The use of compacted mixed compositions of hydrogen-sorbing metals or intermetallic compounds with fullerites makes it possible to deal with this problem. Other advantages of mixed compositions is significant softening of the conditions governing the hydrogenation of the double bonds of the fullerene molecules, the possibility of the multiple repetition of the 'hydrogenation – dehydrogenation' cycle, and the ability of the hydrogenation catalyst to absorb hydrogen. All these factors make the mixtures examined above promising for practical applications.

III. Properties of fullerene hydrides

1. The stability of fullerene hydrides

From the very beginning of the studies on fullerenes, chemists endeavoured to obtain the fully hydrogenated $C_{60}H_{60}$ molecule, but this has not been achieved hitherto.[29, 45, 56, 80–85] As a rule, mixtures of fullerene hydrides are obtained in all the experiments and the main products are usually $C_{60}H_{36}$ and $C_{70}H_{36}$. These polyhydrofullerenes are the most stable also according to theoretical calculations.[47, 58, 102–106] However, even these decompose slowly in solution, which hinders their detailed investigation by spectroscopic methods.[45, 56, 107] Even solid specimens of fullerene hydrides having the same empirical formula but synthesised by different methods exhibit markedly different solubilities, resistances to the action of light and air, capacities for prolonged storage, and other properties ,[29, 45, 59, 61, 80–85] which is apparently induced both by the structural differences between the polyhydrofullerenes themselves and by the presence in the composition of the solid fullerene hydride specimens of different amounts of crystallisation solvents and impurities comprising the components of the catalytic hydrogenation systems, as well as the presence of inhomogeneities and defects in the molecular structure. TGA and emission IR spectroscopy have shown that the fullerene hydrides obtained under the conditions of radical hydrogenation begin to decompose at 350 °C,[61] while the $C_{60}H_{36}$ specimen obtained by Birch reduction [29] began to darken already at 170 °C.

The causes leading to instability of the hydrofullerenes [38, 40, 45, 56] may also be the strain in the newly formed ring as a result of the breakdown of the sp^3 hybridisation of the carbon atoms, the appearance of 5 – 6 double bonds (Fig. 4), and the steric influence of the hydrogen atoms on one another when their number is large.

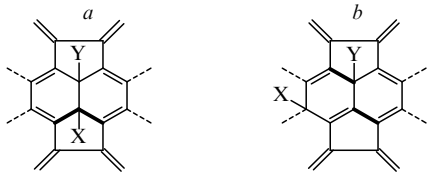


Figure 4. The 1,2- (*a*) and 1,4-addition (*b*) of XY to fullerene.

The instability of $C_{60}H_{60}$ should be associated principally with the deviation of the configuration of the bonds between the carbon atoms from the regular tetrahedral configuration. In this molecule, there are 20 sterically strained cyclohexane fragments on the surface of the sphere. According to the results of molecular-mechanical calculations, the strain may be reduced if at least ten hydrogen atoms in the $C_{60}H_{60}$ molecule are attached endohedrally. This is the most stable conformation for $C_{60}H_{60}$.[108] The difference between the energies of this conformer and the compound in which all the hydrogen atoms are attached exohedrally is 400 kcal mol^{-1}.

The preferred paths in the fullerene halogenation and hydrogenation reactions have been analysed theoretically.[109] Electronic effects are more significant in the interaction of fullerene with fluorine; fluorine adds preferentially in the *ortho*-positions in the 5 – 6 or 6 – 6 bonds, although according to theoretical analysis 1,4-addition (Fig. 4) is also possible. On the other hand, in the interaction of C_{60} with bromine the most stable isomer is formed as a result of 1,4-addition and the direction of the fullerene hydrogenation reaction is intermediate between the directions of the reactions with fluorine and bromine.

2. The state of hydrogen in solid fullerene hydrides

In the direct synthesis of solid fullerene hydrides under a high pressure of hydrogen in the absence of solvents and catalysts, the

formation of the most stable specimens is ensured.[59, 110] Such specimens are most suitable for the study of the nature of the binding of hydrogen by fullerenes in the solid phase. The interest in this problem has been stimulated by the possibility of encapsulating hydrogen molecules either in the intermolecular cavities of the crystal structure of fullerene hydrides or inside the polyhydride carbon framework. These hypotheses are confirmed by the experimental observations made by the investigators of the MER Corporation (USA). The electrochemical cathodic saturation of the C_{60} fullerite with hydrogen results in the formation of compounds containing between 24 and 56 hydrogen atoms per C_{60} molecule and part of this hydrogen is not bound covalently and is readily removed. The conjugation of the double bonds in the fullerene molecule is then retained even for the empirical composition $C_{60}H_{56}$.[28] The synthesis of compounds having the superstoichiometric composition $C_{60}H_{60+x}$ (x reaches 24) by the hydrogenation of fullerite in the region of moderately high temperatures and hydrogen pressures has been reported (without experimental details), the integrity of the carbon framework of the fullerene molecule being retained in these compounds.[111] This intriguing result may imply that under the reaction conditions hydrogen molecules may permeate through the cyclohexane fragments of the shell of the perhydrogenated $C_{60}H_{60}$ fullerene into its inner cavity and may accumulate in the latter. This possibility merits detailed study.

Treatment of C_{60} fullerite with hydrogen (PH = 14 MPa) at room temperature leads only to the formation of an interstitial solid solution of molecular hydrogen, *i.e.* a compound in which the type of packing of the fullerene molecules in the crystal remains unchanged on slight alteration of the lattice parameters.[112] The formation of C–H bonds or new interstitial phases with an altered (compared with the initial fullerite) type of packing of the C_{60} molecules is not observed under these conditions.

In the analogous direct noncatalytic solid-phase synthesis at 600 K, hydrogen actively interacts with C_{60}, giving rise to the hydrides $C_{60}H_x$ = 50–8 MPa)[59] and $x \approx 23$ (at P_{H_2} = 0.6 GPa).[110] The hydrides obtained in this way can be stored for a long time without a significant change in composition and properties. The pressures employed in the above studies [59, 110] did not exceed the threshold value of 0.7 GPa at which the bulk–phase polymerisation of C_{60} fullerene begins at 600 K with formation of C–C bonds between neighbouring fullerene molecules.[113] The temperature of the synthesis was also lower than the initial 950–1000 K level of the temperature range corresponding to the irreversible degradation of fullerene hydrides obtained by different methods.[59, 110] The integrity of the fullerene molecules in the hydrogenated specimens was achieved thereby.[110] The hydrogen content in such specimens is relatively low,[59, 110] but the possibilities for its increase whilst retaining the integrity of the carbon framework of C_{60} have not been fully exhausted.

An attempt has been made [110] to establish the state of hydrogen in fullerene hydride. For this purpose, the chamber with the specimen was cooled after the high-temperature treatment at a high hydrogen pressure [110] and the specimen was extracted directly into liquid nitrogen. The 'quenched' specimen was then heated in a calibrated evacuated space up to 300 K, whereupon the evolution of 2.8 hydrogen atoms per C_{60} molecule was observed. The 'annealed' specimen obtained in this way contained about 23 atoms of covalently bound hydrogen per C_{60} molecule.

Crystallographic data indicate the same type of packing (a body-centred cubic lattice) of the C_{60} molecules in the quenched and annealed specimens. The volume per $C_{60}H_x$ molecule in the annealed specimen is then smaller by 61 Å^3 than in the quenched specimen. Thus the specific volume of the hydrogen evolved on annealing was $61/2.8 \approx 22$ Å^3 per H atom, which is close to the specific volume of solid molecular hydrogen at 4.5 K (19.022 Å^3 per H atom). This fact shows that the hydrogen evolved was present in the quenched specimen in the form of hydrogen molecules occupying the interstitial cavities in the $C_{60}H_x$ lattice. There is evidence that these are not octahedral but tetrahedral interstices in the body-centred cubic lattice.[110]

The state of hydrogen in fullerene hydrides has also been investigated by nonelastic neutron scattering spectroscopic methods.[110] The rotational spectrum of the hydrogen molecules inserted in the interstices obtained at 85 K [110] contains distinct absorption bands corresponding to transitions with the $0 \rightarrow 1$, $1 \rightarrow 2$, and $0 \rightarrow 2$ changes in the rotational quantum number. Thus the inserted hydrogen molecules exist as both para-hydrogen and ortho-hydrogen (at 85 K, their equilibrium ratio is 85 : 15). The rotational spectra of the interstitial hydrogen differ somewhat from those of the free molecules, which is a consequence of the interaction of the hydrogen rotator with the $C_{60}H_x$ ($x \approx 23$) molecules surrounding the cavity. There are similar differences in the rotational spectrum of the molecular hydrogen trapped in amorphous carbon.[114, 115] However, in the latter case, the rotational bands are broader, which apparently indicates the presence of a set of sites where hydrogen molecules are located with different potentials of the interaction with the rotator. On the other hand, in the solid fullerene hydride $C_{60}H_x(H_2)_{1.4}$ ($x \approx 23$) there is apparently one such site.

The vibrations in the low-frequency part of the spectrum (from 0 to 65 cm^{-1}) correspond to the intermolecular interaction in $C_{60}H_x$ ($x \approx 23$).[110] Certain differences in the intermolecular vibrational spectra in solid $C_{60}H_x$ ($x \approx 23$) and C_{60} have been noted. They are due to the anisotropy of the moment of inertia of the $C_{60}H_x$ molecules, leading to the splitting of the libration bands, and also to the much higher dispersion of the libration modes of the hydrogenated C_{60} compared with pure C_{60}. However, despite these slight differences, the C_{60} and C_{60} and $C_{60}H_x$ spectra are extremely similar in this range, which is somewhat surprising bearing in mind the differences between the molecular structures and the types of crystal lattices [simple cubic for C_{60} (77 K) and body-centred cubic for $C_{60}H_x$ ($x \approx 23$)].[110]

3. The structure and isomers of fullerene hydrides

The hydride $C_{60}H_{36}$ was first obtained by an extremely nontraditional method, namely by the Birch reduction of the C=C double bonds. It was therefore postulated that the hydride $C_{60}H_{36}$ contains 12 isolated double bonds in the molecule, one in each five-membered ring.[29] However, subsequently the compounds $C_{60}H_{36}$ were obtained also under other conditions.[45, 56, 61, 80–84] Furthermore, the structure with isolated double bonds for the fullerene hydride $C_{60}H_{36}$ does not explain the inhibition of the reduction after the addition of 36 hydrogen atoms to C_{60}.

The most symmetrical $C_{60}H_{36}$ isomer has 12 double bonds, which are disposed in each five-membered ring and belongs to the T_h symmetry group.[29, 116] The introduction of double bonds into the six-membered rings leads to a structure with a lower point group symmetry T in which there are four benzenoid fragments on the surface of the $C_{60}H_{36}$ molecule located at the corners of the tetrahedron.[102–104] The less symmetrical structures with the D_{3d} and S_6 symmetries,[61, 116] in each of which there are two six-membered rings comprising hydrogen-free carbon atoms located at the poles of the molecule along the threefold axis, are intermediate between these extreme structures. The remaining six double bonds are isolated and disposed along the meridians and parallels of the D_{3d} and S_6 spheres respectively (Fig. 5).

The structures and stabilities of 63 $C_{60}H_{36}$ isomers have been analysed (the total number of $C_{60}H_{36}$ isomers is 6.1×10^{14}, but after the introduction of a series of restrictions, including threefold axes, their number diminishes to 63); one of them has the tetragonal T symmetry, four have the D_{3d} symmetry, three have the S_6 symmetry, nine have the C_{3v} symmetry, and four isomers have the C_3 symmetry.[117] Detailed theoretical analysis of the $C_{60}H_{36}$ structures confirmed that the isomers with the D_{3d} and T molecular symmetries were the most stable.

The relative energies, the electronic structures, and the geometries of four isomers of the $C_{60}H_{36}$ molecule have been calculated by the semi-empirical local density functional (LDF) method (Fig. 5): the symmetries are T, T_h, S_6, and D_{3d}.[105] It was found that the isomer with the T symmetry is energetically the

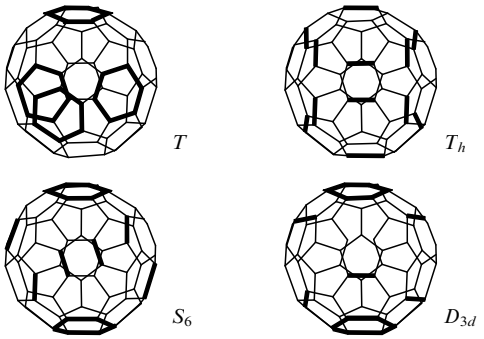


Figure 5. The structural isomers of $C_{60}H_{36}$.[105]

most stable, which agrees with the semi-empirical AM1 calculations,[104] according to which this isomer is more stable than the isomer with the T_h symmetry by 0.7 eV. It may be that the stability of the isomer with the T symmetry, associated with the presence of aromatic rings, is the cause of the inhibition of the more extensive reduction of fullerene.[58] The smallest disruption of the initial fullerene skeleton and the greatest gain of the electron delocalisation energy are characteristic of the structure of the $C_{60}H_{36}$ molecule with the T symmetry. Furthermore, this structure agrees best with the available experimental data.[103] The remaining unsaturated bonds in the isomer with the T symmetry are of the 6–6 type. The ionisation potentials of all the $C_{60}H_{36}$ isomers lie within the range 6.47 ± 0.05 eV and the electron affinity is -0.24 ± 0.03 eV (Table 3).

Theoretical calculations have shown [102–106] that the conjugated structure should be the most stable. It is significant that some of the eight $C_{60}H_4$ isomers, which exist and have been isolated,[38,42] may be built up to the $C_{60}H_{36}$ T isomer on further reduction without any rearrangement of those double bonds of the molecule which are not involved in the reaction. The hydride $C_{60}H_{36}$ may be obtained also by the reduction of the octahedral $C_{60}H_{12}$, which is present among the hydrogenation products.

Since, like $C_{60}H_{36}$, the hydride $C_{70}H_{36}$ is distinguished by a high resistance to further reduction, there may apparently exist common causes which would explain this feature. In particular, steric causes (the mutual repulsion of the hydrogen atoms) should not be decisive in view of the fact that, since 36 hydrogen atoms ensure the maximum stability of the exohedral hydride of the C_{60} fullerene, in the case of C_{70} the maximum number of hydrogen atoms which may be added to the hydrocarbon skeleton without a significant increase in the overall energy should be greater.

In order to account for the characteristic features of the $C_{70}H_{36}$ molecule, structures **A**–**C** have been subjected to a theoretical analysis (Fig. 6).[58]

(1) Structures **A** and **C** have the C_s symmetry, while structure **B** has the C_2 symmetry. The last structure is most uniformly hydrogenated and has 18 hydrogen atoms in each hemisphere of the molecule. (2) The calculated resonance energies suggest that the hydride $C_{70}H_{36}$ exists as a mixture of three isomers and that the compound with structure **B** should predominate, in conformity with its high symmetry. (3) Just as addition to the 9,10-bond in phenanthrene leads to a small change in resonance energy, addition to the analogous bonds of the phenanthrene-like formations in structures **A**–**C** leads to a slight loss of conjugation (80 kJ mol^{-1} for each $C^{16}-C^{17}$ and $C^{28}-C^{29}$ double bond in **A** and $C^{16}-C^{17}$ and $C^{61}-C^{62}$ in **B**; there is a similar loss of 94 kJ mol^{-1} for the $C^{65}-C^{66}$ bond in isomer **C**). The model predicts the formation of $C_{70}H_{38}$ and to a lesser extent of $C_{70}H_{40}$ on further hydrogenation, which has been confirmed experimentally.[56,80,84] (4) Structures **A**–**C** may be obtained by reducing the $C_{70}H_4$ isomers, which really exist.[38,42]

Table 3. Energy characteristics of the $C_{60}H_{36}$ isomers.[105]

Symmetry	Relative energy/eV	Ionisation potential/eV	Electron affinity/eV	HOMO	LUMO
T_h	2.10	6.49	−0.27	$27t_u$	$7a_u$
T	0.00	6.52	−0.21	$17e$	$50t$
D_{3d}	2.35	6.48	−0.23	$33e_u$	$34e_g$
S_6	0.43	6.40	−0.23	$33e_u$	$34e_u$

Further reduction of the stable $C_{60}H_{36}$ and $C_{70}H_{36}$ becomes possible only by overcoming the high energy barrier, which presumably corresponds to the hydrogenation of the six-membered fragments.[58] In this case, the reduction of $C_{60}H_{36}$ should proceed via stepwise hydrogenation with formation of the hydrides $C_{60}H_{36} + n$ (n = 6, 12, 18, 24) and there is experimental evidence for the existence of the compounds $C_{60}H_{42}$ and $C_{60}H_{48}$.[47,83] The reduction of structures **A** and **B** for the composition $C_{70}H_{36}$ should take place via multistage hydrogenation with formation of the hydrides $C_{70}H_{36+n}$, namely $C_{70}H_{46} \rightarrow C_{70}H_{52} \rightarrow C_{70}H_{58} \rightarrow C_{70}H_{64} \rightarrow C_{70}H_{70}$, whereas the reduction of structure **C** should proceed as $C_{70}H_{42} \rightarrow C_{70}H_{46} \rightarrow C_{70}H_{52} \rightarrow C_{70}H_{58} \rightarrow C_{70}H_{64} \rightarrow C_{70}H_{70}$. Since there is a greater loss of resonance energy on formation of $C_{70}H_{70}$ from $C_{70}H_{36}$ ($\sim$1060 or $\sim$31 kJ mol^{-1} for each C=C bond) than on formation of $C_{60}H_{60}$ from $C_{60}H_{36}$ ($\sim$602 or $\sim$25 kJ mol^{-1} respectively), the synthesis of perhydrofullerene $C_{70}H_{70}$ appears even more difficult.[58]

It follows from the foregoing that in principle there may exist three stable $C_{70}H_{36}$ isomers, namely two isomers with two phenanthrene-like and one benzenoid rings and one isomer with one phenanthrene-like and one naphthenoid rings. The increased stability of such structures, associated with the presence of aromatic fragments, prevents their further reduction.

Another study [106] has also been devoted to the question of the stability of various structures of the fullerene hydrides $C_{60}H_{36}$ and $C_{70}H_{36}$. The results of the calculations showed that the formation

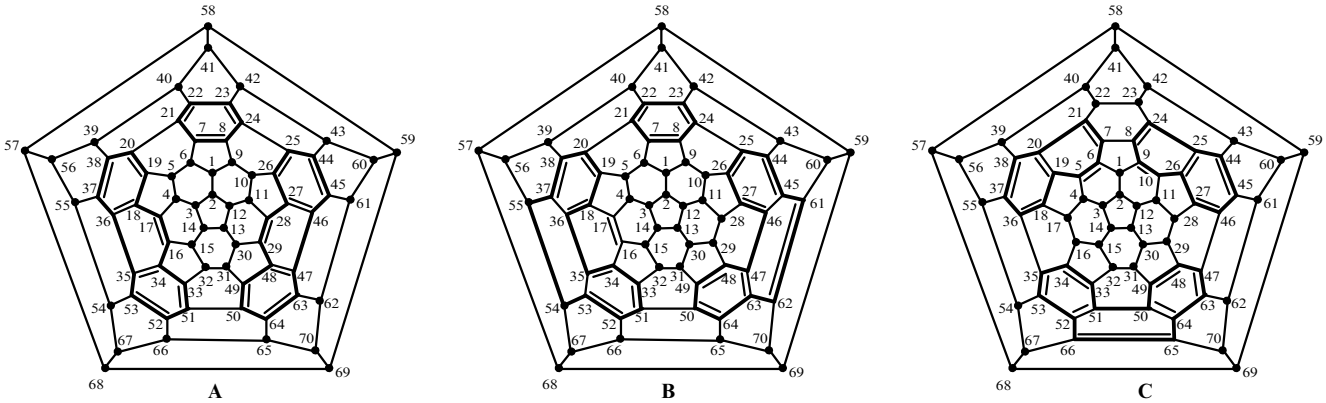


Figure 6. The structural isomers of $C_{70}H_{36}$.[58]

energy of the $C_{60}H_{36}$ isomers with the T symmetry is lower by 97.4 kcal mol^{-1} than the formation energy of the T_h isomer, which confirms the general conclusion reached in other investigations (for example that of Taylor [102]) that the real $C_{60}H_{36}$ structure has the T symmetry. For $C_{70}H_{36}$, structures in which the hydrogen atoms are located at the poles of the molecule in the 1,2,3-positions in the 12 five-membered rings have been considered. Since in this case a graphite-like region with a high degree of conjugation is formed in the equatorial region of the fullerene skeleton, the isomers corresponding to this model should have low formation energies.

The structure of $C_{70}H_{36}$ has also been calculated by methods of molecular mechanics [47] on the assumption that after reduction the reaction product contains only nonconjugated double bonds or double bonds resembling aromatic bonds which are unreactive in relation to hydrogen transfer.[44] In each of the 12 five-membered rings of the carbon cluster, there is one double bond; there is one double bond also at each pole of the $C_{70}H_{36}$ molecule, whilst the remaining ten cyclopentene rings are joined together in such a way that a pentaphenylene strip is formed in the equatorial region. The enthalpy of formation of the hydride $C_{70}H_{36}$ (corresponding to the proposed model) has been calculated as $\Delta H_f^\circ(g) = 490.2$ kcal mol^{-1}. Further reduction of $C_{70}H_{36}$ with formation of $C_{70}H_{40}$ leads to an increase in $\Delta H_f^\circ(g)$ to 535.7 kcal mol^{-1}.

4. Electronic and IR spectra of fullerene hydrides

The lower fullerene hydrides, for example $C_{60}H_2$, retain the C_{60} structure, which is reflected in their UV and visible spectra.[33] A characteristic feature of the formation of the 1,2-addition product is the appearance in the electronic spectrum of bands at $\sim$430 and $\sim$700 nm [39] (436 and 702 nm for $C_{60}H_2$). The formation of $C_{60}H_4$ (the addition of H_2 to the second double bond) is accompanied by the disappearance of the band at 700 nm. The absorption at 220 (230) nm is characteristic of $C_{60}H_{36}$.[29,45] The most detailed spectra of $C_{60}H_{36}$ and $C_{70}H_{36}$, obtained by the reduction of the corresponding fullerenes in a saturated solution in hexane (inert atmosphere) in the Zn/conc. HCl system, have been published by Darwish *et al.*[56] (Fig. 3).

The absorption in the range 255–280 nm has been regarded as evidence for the presence of aromatic fragments of the benzene type in $C_{60}H_{36}$ and of phenanthrene-like fragments in $C_{70}H_{36}$.[58] The presence of these fragments in the fullerene hydride molecule has been demonstrated by the appearance of a charge-transfer band in the spectra of compounds of the type $C_{60}H_{36} \cdot$ TCNE (TCNE = tetracyanoethene).[107]

The IR spectra of the hydrogenated derivatives of fullerenes agree with the presence of C–H and C=C bonds. Thus bands in the region of C–H stretching vibrations are present in the IR spectra of fullerene hydrides (Table 1) — they are weak in the case of the lower hydrides and intense for $C_{60}H_{36}$ and $C_{70}H_{36}$, the number of bands in the case of $C_{60}H_{36}$ depending on the method of synthesis of the hydride. For example, the IR spectrum of the hydride $C_{60}H_{36}$ obtained by radical hydrogenation consists of three intense C–H stretching vibration bands and a weak band at 1490 cm^{-1} band (together with other weaker bands).[61] The bands at 1490, 1511, and 1606 cm^{-1} for $C_{60}H_{36}$ obtained by the transfer hydrogenation [45] lie in the region of the stretching vibrations of the C=C bonds.[61] It has been noted that the intensity of the C=C bond vibration in the region of 1650 cm^{-1} diminishes on reduction under more severe conditions.[83]

For the $C_{60}H_{36}$ molecule with the T_h symmetry, only one active C–H vibration should be observed in the IR spectrum, while for the molecules with the D_{3d} and C_{3i} symmetries one may expect at least 5 and 17 vibrations respectively. ^{13}C NMR data as well as comparison of the experimental and calculated IR spectra for $C_{60}H_{36}$ enabled Attalla *et al.*[61] to reach the preliminary conclusion that the $C_{60}H_{36}$ hydride which they obtained corresponds to the D_{3d} and not the T_h symmetry. At the same time, for a more exact assignment of the IR and NMR bands, the studies should probably be performed on individual specimens of the hydrides of C_{60} and C_{70} fullerenes synthesised by the radical hydrogenation method.

The IR spectrum of the fullerene hydride $C_{60}H_{36}$ obtained by Birch reduction contains bands characteristic of both aliphatic C–H and aromatic C=C bonds.[107] Comparison of the experimental IR spectra with the spectra calculated for the T and T_h structures showed that they are in better agreement with the structure having the T symmetry.[107]

Bands due to the stretching vibrations of the hydrocarbon skeleton in the polyhydride $C_{60}H_x$ containing $\sim$23 H atoms have been identified at 242, 306(s), 453(s), 524, 783, and 912 cm^{-1}. Compared with the vibrations of pure C_{60}, these vibrations have appreciably lower frequencies and differ significantly in the distribution of intensities, which confirms the expected weakening of the C–C bonds and the decrease in molecular symmetry as a result of the hydrogenation of the double bonds. The deformation vibrations of the C–H bonds in the hydride $C_{60}H_{23}$ are characterised by an intense broad ($\Delta\nu_{1/2} = 280$ cm^{-1}) absorption band at 1250 cm^{-1} with a shoulder in the region of 1090 cm^{-1}.[110] A similar peak is characteristic of hydrogenated amorphous carbon,[114,115] which indicates the similarity of the C–H bonds in the two structures.

5. Mass spectrometry in the study of fullerene hydrides

Mass-spectrometric analysis plays a decisive role in the identification of the products of the hydrogenation of fullerenes. The MS analytical methods, differing in the method of vaporisation of the sample and the procedure used for its ionisation, may influence the result, therefore it is necessary to treat mass-spectrometric data with caution. The influence of differences in the analytical method on the results of the analysis has been most fully elucidated in the identification of the products of the Birch reduction of C_{60}.[29,30] The composition of $C_{60}H_{36}$ was first determined from EI-MS data.[29] When the molecules are ionised by fairly soft electron impact in the gas phase, radical-cations are produced with a low internal energy — 2–8 eV (200–775 kJ), which is insufficient for the effective fragmentation of the excited species. This ionisation method is therefore fully suitable for the solution of a series of problems associated with the determination of the molecular structure of the hydride. However, the EI-MS method suffers from a number of disadvantages: in combination with the most readily available method involving vaporisation from a Knudsen cell, it is applicable only to the analysis of thermally stable volatile organic compounds; furthermore, in certain cases the fragmentation of ions with an odd number of electrons, formed on electron impact, proceeds so effectively that the mass spectra contain no molecular ions. The use of the EI-MS and LD-MS methods for the study of $C_{60}H_{36}$ obtained by the radical hydrogenation method proved impossible owing to the thermal decomposition of $C_{60}H_{36}$ to lower-molecular-mass compounds: $C_{60}H_{18}$, $C_{60}H_8$, *etc.*[61] The elimination of hydrogen from the unstable fullerene hydrides ($C_{60}H_n$, $n > 36$) on laser desorption has also been noted by Gerst *et al.*[47]

One of the most important 'mild' and selective ionisation methods is chemical ionisation (CI), which is usually achieved as a result of ion–molecule reactions between neutral molecules of the substances analysed and the ions derived from the reagent gas (methane, isobutane, and ammonia are the most frequently used). The reagent gas ions are as a rule obtained by bombardment with electrons having energies of 100–500 eV at a pressure of $10-10^{-2}$ Pa in the ion source. The collisions of the ions formed with the molecules of the reagent gas result in the formation of reagent ions with an even number of electrons (CH_3^+ and CH_5^+ from methane), which then react with the molecules of the substances analysed. They protonate the molecules of these substances or form adduct ions with them, for example:

$$CH_5^+ + M \longrightarrow CH_4 + MH^+,$$
$$CH_3^+ + M \longrightarrow MCH_3^+.$$

The ions with an even number of electrons generated on chemical ionisation are more stable than the ions with an odd

number of electrons formed on electron impact, so that the mass spectra of the ions generated as a result of chemical ionisation contain the intense peaks due to the adduct ions (or cluster ions) or protonated ions, while the peaks of the fragment ions have low intensities or are absent altogether.

Ionisation methods such as field desorption, secondary ion mass spectrometry, bombardment by fast atoms, laser desorption, *etc*. are also used for the analysis of involatile and thermally unstable compounds.[118] When FD-MS is used, there is no need to vaporise the sample. The sample of solution or suspension is deposited on an activated emitter and the temperature of the latter is chosen to ensure sufficient intensity of the molecular ion peak in the spectrum accompanied by minimal fragmentation (usually 300 – 600 K) Indirect heating of the emitter with the aid of a laser has sometimes proved more effective as regards the formation of molecular ions.

Fullerene hydrides have been studied[45] mass spectrometrically with the aid of various methods, including electron impact, bombardment by fast atoms, and field desorption. M^+ and sometimes M^{2+} peaks are usually present in the $C_{60}H_{36}$, $C_{60}D_{36}$, $C_{60}H_{18}$, and $C_{60}D_{18}$. It has been noted that in the analysis of the above hydrides by the electron impact method, partial fragmentation, accompanied by loss of hydrogen and the appearance of free C_{60}, is observed. The field desorption method gives rise to only the M^+ peak. The FAB method yielded satisfactory results in the analysis of the fullerene dihydride prepared by the reduction of C_{60} with diborane, but its application to other hydride specimens proved difficult (see, for example, Avent *et al*.[38] and Becker *et al*.[87]).

It has been found with the aid of 'mild', mutually complementing mass-spectrometric methods, such as time-of-flight mass spectrometry with vaporisation of the test substance by laser desorption and subsequent laser photoionisation, ion-cyclotron mass-spectrometry with laser desorption, and secondary ion-spectrometry, that a mixture of polyhydrofullerenes with compositions ranging from $C_{60}H_{18}$ to $C_{60}H_{36}$ is indeed formed in the course of the Birch reduction of C_{60}, the main product being $C_{60}H_{32}$.[30] When the L^2TOF-MS method was used to analyse fullerene hydrides in the mass range 740 – 760 a.m.u., the resolution of the instrument proved insufficient for the determination of the mass distribution of the hydrides. Nevertheless, the mass spectrum obtained with the aid of L^2TOF-MS yields no evidence for the formation of $C_{60}H_{36}$ as the main product. The ICR-MS method made it possible to obtain a spectrum with a well resolved series of peaks grouped around the main peak with a mass number of 753 ($752 + H^+$), corresponding to the distribution of the reaction products. The appearance of weak peaks in the range m/z 720 – 730 has been attributed to the fragmentation of the products to low-molecular-mass hydrofullerenes. Finally, the mixture was characterised with the aid of the SIMS method, which yielded a very well resolved spectrum, from which the exact distribution of the hydrogenation products was obtained (Fig. 7).[30]

Thus the difference between the compositions of fullerene hydrides[29, 30] is frequently associated with the difference between the methods used for mass-spectrometric analysis and can be accounted for by the thermal lability of the mixture of hydrogenated fullerenes on prolonged exposure to the high (> 250 °C) temperature necessary for the mass-spectrometric study by the method involving the direct introduction of the heated sample.

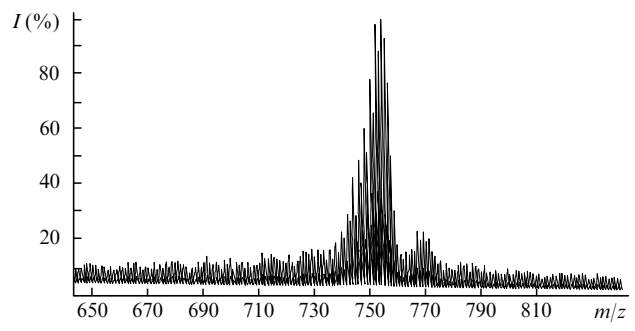


Figure 7. Mass spectrum of the products of the Birch reduction of C_{60} obtained by means of SIMS (matrix — 3-nitrobenzyl alcohol).[30]

6. ^{1}H and ^{13}C NMR spectroscopy

The ^{1}H NMR spectrum of the hydride 1,2-$C_{60}H_2$ contains a singlet at δ = 5.93 ppm (toluene-d_8), which does not change in the range from −80 to 100 °C. On the other hand, there are no well resolved and stable, in terms of time, ^{1}H NMR spectra of either $C_{60}H_{36}$ or $C_{70}H_{36}$. The broad bands with δ in the region from 2.5 to 4.2 ppm and a maximum at 3.80 ppm (for comparison, we may note that δ for dodecahedrane protons is 3.38 ppm), which refer to $C_{60}H_{36}$,[29, 45] agree poorly with the symmetrical structure for which the ^{1}H NMR spectrum should consist of narrow lines.[56] The spectra presented refer as a rule to either mixtures of hydrofullerenes or, if one is dealing with an individual compound, to a mixture of isomers. Finally, the broadening of the bands may be a result of the oxidation of fullerene hydrides by atmospheric oxygen in the presence of light. The attempts to obtain NMR spectra in more concentrated solutions, for example in CS_2 (the CS_2 – C_6D_6 solvent mixture has been used in the case of lower fullerene hydrides of the type $C_{60}H_4$[38]) proved unsuccessful owing to the interaction of CS_2 with $C_{60}H_{36}$[56] observed for the first time in this way. The observation of satisfactory spectra at a low concentration of the test substance requires a long time, which leads to the decomposition of the specimen in the presence of oxygen.

Even in the case of individual C_{60} hydrides, the physicochemical properties of specimens of the same composition but prepared by different methods are different, which may be associated with structural differences.

A complex multiplet with δ = 2.1 – 4.25 ppm is manifested in the ^{1}H NMR spectrum of the catalytic hydrogenation products.[83] A spectrum with δ = 2.5 – 4.5 ppm has been published for $C_{60}H_{36}$ obtained by the Birch method.[29] The appearance of additional signals in the range 2.1 – 2.5 ppm may be associated with the products of the more far reaching hydrogenation of fullerene.[83]

At least four types of sp^3-hybridised carbon atoms with δ = 31, 38, 44, and 49 ppm and three types of sp^2-hybridised carbon atoms with δ = 128, 134, and 138 ppm are manifested in the solid-state ^{13}C NMR spectra of a reduced mixture of C_{60} and C_{70}.[61] Integration yields the ratio $sp^2 : sp^3 \approx 22 : 38$. When account is taken of the integration error, this ratio corresponds satisfactorily to the presence of a hydride with 36 hydrogen atoms. Analysis of the ^{13}C NMR spectrum led the authors[61] to the conclusion that a structure with the D_{3d} symmetry may be assigned to the compound $C_{60}H_{36}$.

The structure of the hydride $C_{60}H_{36}$ formed on Birch reduction of C_{60} has also been investigated by Govindaraj.[107] The results agree with the data of Haufler *et al*.[29] but their interpretation is different. Thus the ^{13}C NMR spectrum of the hydride $C_{60}H_{36}$ obtained by the Birch method contains signals with δ = 140 and 40 ppm, which Govindaraj[107] assigns to aromatic and saturated carbon atoms respectively. The signals of the carbon atoms in the aromatic ring proved weaker than might have been expected (apparently owing to the quaternary nature of these atoms). According to Govindaraj,[107] these spectra confirm a structure with the T symmetry for $C_{60}H_{36}$. The UV spectrum of this compound contains bands at 218 and 275 nm. Govindaraj[107] believes that the band at 275 nm indicates the presence of an isolated aromatic fragment in the $C_{60}H_{36}$ molecule (see also Darwish *et al*.[56]). The presence of such an isolated benzene ring is demonstrated by the appearance of a charge-transfer band (305 nm) when $C_{60}H_{36}$ interacts with tetracyanoethene[107] (in the benzene – TCNE system, the charge-transfer band is at ~300 nm[119]). It has been suggested that the hydride $C_{60}H_{36}$ with the T symmetry and having isolated double bonds is formed initially during the hydrogenation reaction and is then transformed via sigmatropic shifts into a thermodynamically more stable molecule

with the T symmetry and isolated benzene rings. This hypothesis has been confirmed by the synthesis by the method of Rüchardt *et al.*[45] of a $C_{60}H_{36}$ specimen stable in the solid state.

The ^{3}He chemical shifts in the ^{3}He NMR spectra of the possible isomers of the endohedral complexes $He@C_{60}H_{36}$ have been calculated.[62] The calculated shifts for different isomers (the type of symmetry is indicated in brackets) of $He@C_{60}H_{36}$ are $-10.8(T)$, $-7.4(D'_{3d})$, $-6.1(S_6)$, $-3.4(T_h)$, and -5.6 ppm (D_{3d}).[62] The calculation also confirmed that the chiral structure with the T symmetry is the most stable among the possible $C_{60}H_{36}$ isomers (the T structure is more stable than the T_h structure by 59 kcal mol^{-1}). The authors [62] suggest that the experimental investigation of compounds of the type $He@C_{60}H_{36}$ will yield new information about the composition of the C_{60} hydrogenation products.

7. Photophysical properties of fullerene hydrides

The photophysical properties of three hydrofullerenes have been investigated at room temperature in solution in toluene: $C_{60}H_2$, $C_{60}H_4$, and 2,3-[1-(3-carboxypropionyloxymethyl)-4-methylbut-2-eno]buckminsterfullerene **2** (the last compound has a hydrophilic substituent linked to the hydrophobic C_{60} skeleton).[120] The visible absorption spectra of these compounds in the ground state were compared with the spectra of methanofullerenes and methanofulleroids.¶ The changes observed in the spectra of methano- and hydro- fullerenes compared with the spectra of C_{60} and methanofulleroids are associated with the differences between the electronic structures of these molecules (58 and 60 π-type electrons respectively). The absorption spectra of $C_{60}H_2$, $C_{60}H_4$, and compound **2** in the triplet state are similar ($\lambda_{max} \approx 700$ nm for $C_{60}H_2$ and compound **2** and $\lambda_{max} \approx 710$ for $C_{60}H_4$). The quantum yield in the formation of the photosensitised $^1O_2(^1\Delta_g)$ in the presence of $C_{60}H_2$, $C_{60}H_4$,and compound **2** is close to unity, as in the case of C_{60}. The high effectiveness of the generation of singlet oxygen is probably the cause of the frequently observed degradative changes in the structures of fullerene hydrides in solution.[33, 45, 56] The molar absorption coefficients of $C_{60}H_2$, $C_{60}H_4$, and compound **2** in the excited triplet state have been calculated as $\sim$10 500 (at 700 nm), $\sim$4800 (at 710 nm) and $\sim$11 000 mol litre^{-1} cm^{-1} (at 700 nm) respectively.

8. The acidity and strength of the C–H bonds in fullerene hydrides

The voltammetric method has been used to investigate the acid–base reactions of hydrogenated fullerenes in solution in dimethyl sulfoxide (DMSO).[121] According to Guarr *et al.*[122] and Boulas *et al.*,[123] dihydrofullerene $C_{60}H_2$ gives rise to three reversible reduction peaks (the radical-anion, dianion, and trianion) with potentials approximately 0.1 V more negative than the corresponding potentials of C_{60} in the 67 : 33 (by volume) DMSO–toluene mixture. It was noted that $C_{60}H_2$ decomposes slowly in this medium to C_{60}. A series of bases were used to deprotonate $C_{60}H_2$ and to determine the acidity.

$$C_{60}H_2 + B^- \rightleftharpoons C_{60}H^- + BH,$$

$$K_1 = \frac{[C_{60}H^-]\,[BH]}{[C_{60}H_2]\,[B^-]}\ .$$

(B^- represents the sodium salts of dichloroacetic acid, saccharin, and trifluoroacetic acid; the pK_a for these acids in DMSO are 6.4, 4.0, and 3.45 respectively).

The values of pK_a (1) and pK_a (2) (for the first and second dissociation constants) found for $C_{60}H_2$ are 4.7 and 16 respectively (DMSO, 298 K). The acid dissociation constant of the C–H bond in Bu^{t}C$_{60}$H is 5.7.[124] The replacement of the *tert*-butyl group by hydrogen leads to an increase in acidity by virtue of the stronger electron-donating character of the *tert*-butyl group compared with hydrogen.

By employing the sensitivity of the absorption band of the complex of the $C_{60}^{\bullet -}$ radical-anion and γ-cyclodextrin (γ-CD) at 1080 nm in the near IR, the pK_a of the conjugate acid $(C_{60}H)^{\bullet}$ was determined in the 9 : 1 H_2O–Pr^{i}OH mixture and was found to be 4.5 (±0.5).[125]

$$(C_{60}H)^{\bullet}\cdot\gamma\text{-CD} \rightleftharpoons C_{60}^{\bullet -} + H^+.$$

A pK_a of the same order of magnitude has been quoted for $HC_{60}^{\bullet}$ in dichlorobenzene.[126] On the other hand, in DMSO the value pK_a = 9, was obtained for $HC_{60}^{\bullet}$ by Niyazymbetov *et al.*[121] The high acidity of $HC_{60}^{\bullet}$ is combined with a low strength of the C–H bond (71 kcal mol^{-1} for Bu^{t}C$_{60}$H).[124] We may note that quantum-chemical calculations yield C–H bond energies in $C_{60}H_{12}$ (73 kcal mol^{-1}) and $C_{60}H_{18}$–$C_{60}H_{36}$ (70–71 kcal mol^{-1})[104] which are close to the experimental C–H bond strengths in fullerene monohydride.[124] The calculated average C–H bond energy in $C_{60}H_{60}$ is $\sim$62 kcal mol^{-1}. Such a decrease is caused by the significant structural strain in the fully saturated hydrocarbon framework.[104]

Electrolysis of C_{60} to give C_{60}^{2-} with subsequent protonation constitutes an alternative free-radical method of synthesis of $C_{60}H_2$.[126] The stepwise protonation of the dianion showed that the first proton adds more readily than the second.

An attempt has been made to create a pK_a scale for the hydrofullerene series.[127] The calculated acidities confirm the hypothesis [2] that the acidity of fullerene hydrides diminishes with increase in the degree of hydrogenation. In this sense, fullerene monohydride $C_{60}H$ should have the most acidic aliphatic C–H bond.

9. X-ray photoelectron spectroscopy in the study of fullerene hydrides

The fullerene hydride $C_{60}H_{36}$ synthesised by reducing C_{60} with dihydroanthracene in the melt [45] has been investigated by electron energy loss spectroscopy (EELS).[128] Fig. 8 presents the loss functions for $C_{60}H_{36}$ and C_{60}. Both functions have a similar form, but the maximum due to the oscillations of all the valence electrons [the (σ + π)-plasmon] is located at a lower position as regards energy in the case of the hydride (23.8 eV) than in the case of solid C_{60}(25.0 eV). This means that the valence electron density, determined by the magnitude of this energy, diminishes on passing from C_{60} to $C_{60}H_{36}$. The relative intensity of the peak associated with the excitation of the π-plasmon also decreases appreciably in this transition. Under these conditions, the π-plasmon peak loss energy hardly changes. With increase in the irradiation time, the form of the loss function for $C_{60}H_{36}$ becomes similar to that of the function for C_{60}, which is apparently associated with the evolution of hydrogen from the hydride.

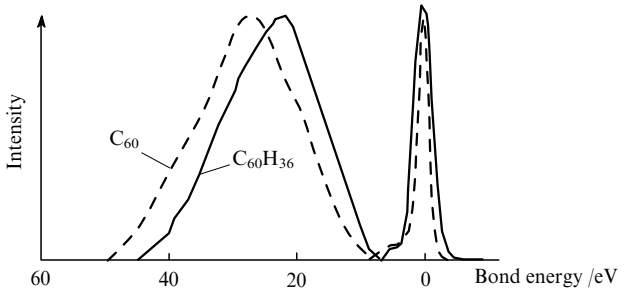


Figure 8. The loss functions for the hydride $C_{60}H_{36}$ (continuous line) and fullerene (dashed line) in the EELS spectra.[128]

10. Electrochemistry of fullerene hydrides

In many respects, the electrochemical behaviour of $C_{60}H_2$ is similar to the behaviour of C_{60} fullerene, but $C_{60}H_2$ is reduced

¶ Methanofullerenes and methanofulleroids differ in the way that the ligand is attached to the double bonds of fullerene: addition to the 6–6 bonds with retention of the fullerene framework and the formation of a cyclopropane ring in the former case and the opening of the 6–5 bond in the case of methanofulleroids.

with somewhat greater difficulty.[122] The potentials $E_{1/2}$ for the reduction of $C_{60}H_2$ in various solvents are presented in Table 4.[122]

Table 4. Electrochemical reduction of $C_{60}H_2$.[122]

Solvent [a]	$E_{1/2}$ ($C_{60}H_2^{z-}/C_{60}H_2^{(z+1)-}$) /V rel. to Fc^+/Fc			
	0/1−	1−/2−	2−/3−	3−/4−
PhMe–CH_3CN	−1.05	−1.44	−1.99	−2.36
PhCN	−1.04	−1.43	−2.01	
CH_2Cl_2	−1.11	−1.48	−1.99	

[a] 0.1 M $(C_4H_9)_4NPF_6$ was used as the electrolyte.

The electrochemical properties of $C_{60}H_2$ and 1.9- and 7.8-$C_{70}H_2$ in the DMF–toluene mixture have been investigated.[123] $E_{1/2} = -1.02$, -1.46, -2.07, and -2.58 V (relative to Fc/Fc^+) have been obtained for $C_{60}H_2$. Owing to the lower solubility of the reduced $C_{70}H_2$ isomers in the DMF–toluene mixture, it is possible to observe only three consecutive electron transfers for these substances. Thus $E_{1/2} = -1.04$, -1.48, and -1.96 V (relative to Fc/Fc^+) have been obtained for 7,8-$C_{70}H_2$, while the corresponding values for 1.9-$C_{70}H_2$ are -1.03, -1.52, and -1.93 V. The electronic effects in these isomers, having different stabilities, are not reflected in their electrochemical behaviour. The stability of the reduced hydride derivatives decreases with increase in the charge, temperature, and (or) the content of DMF in the DMF–toluene mixture. The singly charged radical-anion $C_{60}H_2^-$ proved to be the most stable among the reduced compounds (the EPR spectrum of $C_{60}H_2^-$ is characterised by $g = 2.000$ and $\Delta H = 3$ G at 160 K, whereas the EPR spectrum of C_{60}^- has $g = 1.997$ and $\Delta H = 5.8$ G).[123]

The electrochemical oxidation of $C_{60}H_2$ has been investigated in PhCN. It is irreversible and takes place in two stages. In the first stage, C_{60} is formed from $C_{60}H_2$ as a result of the loss of two protons and two electrons, and then oxidised in the second stage at more positive potential ($E_p = 1.13$ and 1.35 V relative to Fc/Fc^+).

11. Reactions of fullerene hydrides

The anion $C_{60}H^-$ exhibits fairly strong nucleophilic properties. It is formed when stoichiometric amounts of C_{60} and $LiBEt_3H$ are mixed in toluene.[129] Methyl iodide does not alkylate this compound,[129] whereas $Et_3O^+BF_4^-$ in dichloromethane reacts with $C_{60}H^-$ to form 1,2-C_{60}(H)(Et) in a quantitative yield. The ^{1}H NMR spectrum of the product of the reaction of $C_{60}H^-$ with $Et_3O^+BF_4^-$ in CS_2–$CDCl_3$ [$\delta = 6.42$ (s, 1 H, C_{60}H), 3.50 (q, 2 H, CH_2), 2.09 (t, 3 H, CH_3)][130] agrees with that described by Hirsch *et al.*[131] The anion $C_{60}H^-$ is protonated by HBF_4 in ether with formation of 1,2-$C_{60}H_2$, giving rise to a singlet at $\delta = 5.93$ in toluene-d_8.[130]

The addition of nucleophiles to unsaturated ligands in cationic metal complexes, well known in organometallic chemistry, proceeds smoothly also in the reaction with $C_{60}H^-$, the unsaturated ligands serving as a bridge between fullerene and the metal.[130]

$$[(OC)_5Re(\eta^2\text{-}C_2H_4)]^+ + C_{60}H^- \longrightarrow 1,2\text{-}C_{60}(H)(-CH_2CH_2-)Re(CO)_5,$$

$$[(OC)_3Fe(\eta^5\text{-}C_6H_7)]^+ + C_{60}H^- \longrightarrow 1,2\text{-}C_{60}(H)(-\eta^4\text{-}C_6H_7-)Fe(CO)_3,$$

$$[(OC)_3Fe(\eta^5\text{-}C_7H_9)]^+ + C_{60}H^- \longrightarrow 1,2\text{-}C_{60}(H)(-\eta^4\text{-}C_7H_9-)Fe(CO)_3,$$

$$[(OC)_5Mn(\eta^6\text{-}C_6H_6)]^+ + C_{60}H^- \longrightarrow 1,2\text{-}C_{60}(H)(-\eta^5\text{-}C_6H_6-)Mn(CO)_3,$$

$$[(\eta^5\text{-}Cp)Fe(\eta^6\text{-}C_5H_4CH_2)]^+ + C_{60}H^- \longrightarrow$$
$$\longrightarrow 1,2\text{-}C_{60}(H)(-\eta^5\text{-}CH_2C_5H_4-)Fe(Cp\text{-}\eta^5).$$

The ^{1}H NMR spectra of these complexes exhibit a signal in the range $\delta = 5.9$–6.5 ppm, characteristic of the compounds 1,2-C_{60}(H)(R).[3, 132] The mass spectra of the products indicate that the molecular ions 1,2-$C_{60}(H)(RML_x)^{+\bullet}$ decompose mainly via the β-elimination mechanism with formation of C_{60}^+. The compound 1,2-C_{60}(H)[$CH_2CH_2Re(CO)_5$] decomposes as a result of double β-elimination to C_{60}^+, $H_3CCH_2Re(CO)_5^+$ and $HRe(CO)_5^+$. Thus a convenient method has been proposed [130] for the synthesis of metal complexes in which fullerene is linked to the metal atom not directly but via a carbon bridge.

IV. Conclusion

The history of the study of fullerene hydrides covers only a few years, but, despite the preliminary nature of many investigations and the controversial character of certain conclusions, it is already clear that a long life in science and technology lies ahead of this field. The report concerning the study of the structure of the individual hydride $C_{60}H_{18}$ by the ^{1}H NMR method may be regarded as a consecutive advance in this direction.[133] The hydride $C_{60}H_{18}$, obtained by the solid-phase hydrogenation method, has the C_{3v} symmetry according to ^{1}H NMR data. The study by the differential scanning calorimetry (DSC) of the thermal stability of the highly pure $C_{60}H_{36}$ showed that, together with the dehydrogenation of $C_{60}H_{36}$ to C_{60}, processes involving the degradation of the carbon skeleton of the fullerene take place.[134]

The great potential possibilities for the practical employment of systems based on fullerene hydrides have also promoted the rapid development of the relevant research. One may postulate the possibility of creating electrochemical cells employing intermetallic compounds — fullerene hydride compositions as cathodic materials, as well as the creation of reversible hydrogen accumulators.

The possibility of employing a wide temperature range and of the chemical modification of fullerenes makes it possible to regulate their reactivity in relation to hydrogen. This is of fundamental importance for the creation of active catalysts of the reactions of hydrocarbons. For example, the crystalline adducts of fullerenes with alkali metals, certain representatives of which (M_3C_{60}) exhibit superconducting properties, are capable of catalysing effectively even at -100 °C the homonuclear isotope exchange of hydrogen.[135] At 300 K and a pressure of the $H_2 + D_2$ mixture of 100 Torr, the reaction rate constant for the Cs_6C_{70} catalyst is 10 min^{-1}. It is 60 times greater than for the caesium compound of graphite having the same composition. The activation energy for the reaction is 11.1 kJ mol^{-1}. In the presence of the Cs_6C_{70} catalyst, ethene is hydrogenated by hydrogen already at 373 K and the rate constant at a pressure of the $C_2H_4 + H_2$ mixture of 200 Torr is 0.5 min^{-1}. The proposed process mechanism involves the dissociative adsorption of the H_2 molecule on the hydrocarbon framework with formation of fullerene hydrides (H_2 is activated similarly on the noble metals platinum and palladium).[135]

The dehydrogenating activity of fullerene catalysts in relation to alkanes,[50] including methane,[52, 53] exhibited in the range of high temperatures, as well as the influence of hydrogen on the dehydrogenation process similar to that of catalysts based on noble metals,[53] makes it possible to regard fullerene catalysts as functional analogues of noble metals. The possibility of a wide variation of the composition of fullerene-containing catalysts and of the temperatures at which they are used makes fullerene structures promising catalysts for a wide variety of reactions of saturated hydrocarbons such as reforming, hydrocracking, dehydrogenation, and others of great industrial importance.

Catalysis with particiption of fullerene hydrides may contribute to the recombination of hydrogen atoms with formation of H_2 occurring in interstellar space.[136] This fundamental hypothesis may be tested with the aid of laboratory studies of the absorption and emission spectra of fullerenes in the UV and IR ranges and by comparison with the spectroscopic characteristics of interstellar space. Another stage in testing the hypothesis may be the laboratory study of the possibility of achieving the bimolecular reaction involving the addition fullerene skeleton with radiation cooling of the excited adduct. Only the readily occurring termolecular addition of a hydrogen atom has now been demonstrated experimentally.[136]

The problem of the reduction of fullerenes continues to interest investigators. The electrochemical hydrogenation of C_{60} in 30% aqueous KOH solution has been achieved.[137] The cathodic C_{60} reduction potential has been found to be -1.4 V (relative to Ag/AgCl). It has been shown that $C_{60}H_2$ is formed under these conditions, although the yield of the dihydride is low. The hydrogenation of C_{60} and the dehydrogenation of $C_{60}H_x$ during electrolysis are reversible.

$$C_{60} + x\,H_2O + x\,e^- \rightleftharpoons C_{60}H_x + x\,OH^-.$$

Thus the possibility of using C_{60} as the electrode material for the creation of batteries in aqueous KOH has been demonstrated.

Preliminary results of the study of the reduction of higher (C_{76}, C_{78}, and C_{84}) fullerenes in the Zn–conc. HCl–toluene system in the dark and in the absence of oxygen have been reported.[138] The reduction of C_{76} leads to $C_{76}H_{46}$–$C_{76}H_{56}$, while the reduction of C_{78} (according to the isomeric composition of the initial fullerene) affords a wide range of hydrogenation products, $C_{78}H_{48}$ being the main component. Products having the compositions $C_{84}H_{48}$–$C_{84}H_{52}$ have been obtained as a result of the reduction of C_{84}. In each case, the reduction of higher fullerenes is accompanied by the degradation of the specimen and the appearance of the hydrides $C_{60}H_{36}$ and $C_{70}H_{36}$ and $C_{70}H_{40}$ (HPLC), which confirms yet again that the stability of these hydrides is a maximum and that the reduced C_{84} derivatives are least stable.

The photochemical reaction ($\lambda = 350$ nm, N_2, 12 h) of C_{60} with tertiary amines $RNMe_2$ (R = Ph, Me) leads to products of the addition of the amine to the 6–6 bond of the fullerene.[139] On further irradiation of the reaction mixture in the presence of an excess of C_{60}, the adduct is converted into a pyrrolidine derivative of C_{60} and 1,2-$C_{60}H_2$, confirming thereby the possibility of reducing the fullerene when mixtures of fullerenes with organic compounds are irradiated.

The theoretical analysis of fullerene hydrides has been continued.[140, 141] Structures with a skewed pentagonal-pyramidal disposition of hydrogen atoms have been considered. The addition of hydrogen to $C_{60}H_6$, $C_{60}H_{12}$, or $C_{60}H_{18}$ takes place mainly in the *ortho*-position, whereas the addition of bromine occurs preferentially in the *para*-position. Hydrogen and bromine are eliminated respectively from the *para*- and *ortho*-positions in one of the skewed pyramidal structures. The pentagonal-pyramidal $C_{60}H_6$, the doubly pentagonal-pyramidal $C_{60}H_{12}$, the triply pentagonal-pyramidal $C_{60}H_{18}$ and also $C_{60}H_{26}$, $C_{60}H_{28}$, and $C_{60}H_{36}$ do not disproportionate to higher and lower hydrides.

It has been shown with the aid of IR and ^{1}H NMR spectroscopy that, in the interaction of C_{60} with $HIr(C_8H_{12})(PPh_3)_2$ the transition metal atom is coordinated to the C_{60} molecule via the C^1–C^2 bond.[142]

It has been shown [143] that in the absence of oxygen in the dark and on irradiation, the interaction of C_{60} with $H_3Ir(PPh_3)_3$ leads to different products: to the complexes of iridium with η^2-coordinated C_{60} on heating in toluene (100 °C) and to the oxidation of iridium by the triplet-excited C_{60} (Nd^{3+} : YAG laser, $\lambda = 532$ nm) on irradiation in benzonitrile. The photochemical reaction in benzonitrile leads to the appearance of an absorption band in the near IR and of an EPR signal for the C_{60} radical-anion ($\lambda = 1078$ nm, $g = 2.0001$). The triplet-excited C_{60} is quenched by the complex $H_3Ir(PPh_3)_3$ *via* a reductive mechanism, the quenching constant being $k_g = 1.1 \times 10^9$ mol^{-1} s^{-1}.

It has been noted [144] that the appearance of a signal with m/z 780 (see, for example, Shigematsu *et al.*[83]) in the mass spectrum of the C_{60} hydrogenation products when toluene is used as the solvent is probably associated with the formation of the trimethylene adduct of the fullerene hydride $C_{60}H_{18}$ and not with the formation of $C_{60}H_{60}$.

The optimum structures and the relative stabilities of the $C_{70}H_{36}$ molecule (the heats of formation of the isomers) have been calculated, which showed that the presence of aromatic fragments on the surface of the molecule is not the dominant factor determining the stability. The energy of the deformation of the molecule owing to steric strain, induced by the fact that aromatic fragments must be planar, exceeds the resonance energy gained. A series of structures have already been proposed for $C_{70}H_{36}$ with partly isolated double bonds,[145] their calculated heat of formation being significantly lower than for the 'aromatic' isomers. The search for the optimum combination of aromaticity and steric strain in $C_{70}H_{36}$ isomers is being continued.[146]

The photophysical properties of the hydrides $C_{60}H_{18}$ and $C_{60}H_{36}$, obtained with a purity of 90%–98% by the transfer hydrogenation [45] with subsequent purification by sublimation,-differ significantly.[147] The absorption spectrum for the ground state of $C_{60}H_{36}$, measured in solution and in methylene chloride, indicates the presence of isolated benzenoid fragments in the structure of the hydride. They are present in the isomers with the T, S_6, or D_{3d} point symmetry group and are absent from the most symmetrical T_h isomer. Furthermore, the energy calculated for the molecule with the T_h symmetry is higher by more than 2 eV than the energy of the most stable-isomer.[105] Additional information about the symmetry of $C_{60}H_{36}$ is provided by the group-theoretical study of the IR and Raman spectra of the specimens obtained and also by the solid-phase ^{13}C NMR spectrum, which contains signals due to several different sp^3-hybridised carbon atoms instead of the single signal expected for the T_h structure.[147] Analysis of the entire set of data enabled the authors [147] to reject the T_h structure for $C_{60}H_{36}$ and to identify the structure with the S_6 symmetry as the most probable. This conclusion differs from the conclusion by the authors of earlier studies [61, 112] that the $C_{60}H_{36}$ specimens obtained by direct hydrogenation at a high pressure have the D_{3d} symmetry. These were investigated by electron and X-ray diffraction and also with the aid of NMR and IR spectroscopy, the spectroscopic characteristics of the specimens differing significantly from those obtained by Bensasson *et al.*[147] These differences have been interpreted [147] as evidence that different synthetic methods afford $C_{60}H_{36}$ isomers having different symmetries.

However, within the limits of one method products with different isomeric compositions can apparently be formed. Thus the hydrogenation of C_{60} by 9,10-dihydroanthracene,[148] analogous to that described by Bensasson *et al.*[147] leads to a product containing as the main component the $C_{60}H_{36}$ isomer with the T symmetry. Its solid-state ^{13}C NMR spectrum contains three signals due to sp^3-hybridised carbon atoms at 31.1, 37.2, and 44.1 ppm and three signals due to sp^2-hybridised carbon atoms at 124.9, 134.7, and 137.3 ppm with an integral intensity ratio of 36 : 24.[148]

The electronic absorption spectrum of $C_{60}H_{18}$ in the ground state differs greatly from the spectrum of $C_{60}H_{36}$ [147] and its structure is very close to that of the spectrum of C_{60}, which suggests the presence in the $C_{60}H_{18}$ molecule of an analogous conjugation system of sp^2-hybridised carbon atoms, but with the difference that they do not cover the entire surface of the sphere.[147] This agrees with the results of the analysis of the ^{1}H NMR spectra of $C_{60}H_{18}$ specimens obtained by the solid-phase hydrogenation method.[133] The absorption spectrum of the lowest $C_{60}H_{18}$ triplet, obtained by flash photolysis in benzene,[147] is also structurally very similar to the spectrum of the triplet–triplet absorption of C_{60} in benzene and is located in the identical wavelength range, which confirms the postulate that the type of conjugation present in the initial C_{60} is retained to a significant extent in $C_{60}H_{18}$. An additional argument in support of this claim is the similarity of the lifetimes of the lowest $C_{60}H_{18}$ triplet (210 μs)[147] and C_{60} (47 μs) in benzene. The quantum yield in the formation of the triplet $\varphi_t(C_{60}H_{18}) < 0.12$, estimated from the results of the flash photolysis of solutions in benzene, is appreciably lower than $\varphi_t \approx 1$ for C_{60} and the lowest hydrides $C_{60}H_2$ and $C_{60}H_4$.[120, 147] This fact agrees with the very weak fluorescence of C_{60}, $C_{60}H_2$, and $C_{60}H_4$ (the quantum yield of the C_{60} fluorescence is $\approx 10^{-4}$) compared with the fairly intense fluorescence of $C_{60}H_{18}$.[147] Such modification of the photophysical properties as a result of the increasing hydrogenation of the carbon framework of C_{60} may be of interest for medicine, biology, and photonics. Unfortunately, the photophysical characteristics of the triplet state of $C_{60}H_{36}$ could not

be measured: the triplet–triplet absorption spectrum of this compound in the wavelength range accessible to measurements ($\lambda > 300$ nm) is lacking.

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