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REACTION OF HEXAFLUOROBENZENE AND TETRADECAFLUOROHEXANE WITH LITHIUM AMALGAM

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SUMMARY

Hexafluorobenzene and tetradecafluorohexane in the gas phase react spontaneously with lithium amalgam, already at room temperature to give a solid and intimate mixture of lithium fluoride and elemental polymeric carbon with a small amount of superstoichiometric lithium. The reaction can be elucidated by an electrochemical corrosion mechanism. The reaction product was studied by organic elemental analysis, X-ray diffraction, X-ray photoelectron spectroscopy and infrared spectroscopy. The elemental carbon is electronically conducting, highly disordered and reactive towards oxygen.

INTRODUCTION

The outstanding stability of perfluorinated polymeric materials against most chemical reagents is well-known and utilized in practice. For example, poly(tetrafluoroethylene) (PTFE) is chemically attacked only by alkali metals, fluorine, ClF_3 , and some highly reactive organic radicals, such as naphthalenides [1,2]. This polymer can be, on the other hand, quite easily reduced electrochemically on lead or platinum electrodes in aprotic solvents [3] or by electrochemical corrosion with alkali metal amalgams [4,5] . The latter reaction proceeds most rapidly with lithium amalgam, and its product is a solid and compact mixture of LiF and elemental carbon containing a small amount of chemically bound lithium [6] . The reaction of lithium amalgam and PTFE can be understood as an electrochemical process in a galvanic cell with a lithium amalgam anode and PTFE functioning as a cathodic depolarizer:

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Li(Hg) | C-LiF | C-PTFE .

The reaction takes place at the carbon cathode (interface between the product C-LiF and PTFE). The reduction product C-LiF has the properties of a solid electrolyte with mixed electronic and ionic conductivity, the transport number for Li^+ being 1. This product acts also as a separator of electrodes, and, on the other hand, closes the electrical circuit of the cell [4,5,7] .

The prepared elemental carbon possesses an unusual ("carbyne") structure [8-10] , extreme chemical reactivity [11-13] and adsorption capacity [7,14] , and interesting electrical [15] and other physico-chemical properties [16,18] . This topic was also reviewed recently [19] .

Electrochemical reduction of other fluoropolymers with lithium amalgam was also studied. Sulphonated fluoropolymer Nafion 117 (duPonts trade mark) reacts in a similar way to give a carbon material containing intact sulphonic groups [20] . Less detailed data are also available for other fluoropolymers, such as Kel-F, Fluoropak 80 and Ribbon Dope P 412 [21] . Partly fluorinated polymers are, however, less stable than perfluorinated, e.g. poly(vinylidene fluoride) can be converted to elemental carbon already by chemical dehydrofluorination with various bases in dimethylformamide solution [22] .

Till present, only electrochemical reduction of solid fluoropolymers with lithium amalgam was studied. The aim of this paper is to investigate the reaction of lithium amalgam with small perfluorinated molecules in the gas phase. We chose two model substances: perfluorohexane as an example of a very short perfluorinated hydrocarbon chain (in comparison with PTFE), and perfluorobenzene as an example of 'infinite long', cyclic perfluorinated hydrocarbon chain. The present work shows that these small molecules can be reduced electrochemically to elemental carbon and LiF like poly-(tetrafluoroethylene).

RESULTS AND DISCUSSION

Reaction of C_6F_6 and C_6F_{14} with lithium amalgam

Both perfluorinated reactants react spontaneously with lithium amalgam already at room temperature. Immediately after the first contact of the reactant vapour with the amalgam surface, its metallic gloss disappears and a layer of reaction products begins to grow. During the first 10 - 20 minutes, the amalgam surface exposed to the reactant vapour changes its colour in the sequence: violet -

green - yellow, and this process repeats several times. Finally, the colour of the product layer turns black. The observed colour effects are apparently caused by reflection and interference of white light on thin layers in the early stages of the reaction. These thin layers are very uniform and without defects, because the interference colours are observed on the whole surface of the exposed amalgam, without strips or circles. After several days of reaction, a black, compact body of reaction products results. This cover layer separates perfectly the amalgam from the reactant vapour and is mechanically stable even during leaning or revolving the apparatus. It can be destroyed only by intensive shaking of the amalgam.

The consumption of lithium metal was studied at various reaction conditions and the results are summarized in Table 1.

TABLE 1

Yield of the reaction of C_6F_x (x = 6, 14) with lithium amalgam at various conditions. The consumption of lithium in mg and in per cent of actual amount of Li taken into the reaction is indicated.

Temperature (°C)	Time (days)	Shaking	C_6F_6-Li (mg)	C_6F_6-Li (%)	C_6F_{14}-Li (mg)	C_6F_{14}-Li (%)
25	5	No	1.70	3.21	1.94	3.52
25	25	No	5.04	9.33	7.01	13.2
25	1	Yes	55.4	97.0	54.3	99.1
60	3	No	53.8	100	54.3	100
80	2	No	56.8	100	-	-

It is apparent that at higher temperatures or by shaking at room temperature, lithium amalgam can quantitatively be converted to a carbonaceous product during 1 - 3 days. The products were washed with 5 x 500 ml of water in contact with air and powdered carbon materials, further denoted as C/benz (from C_6F_6) and C/hex (from C_6F_{14}) were isolated. The water extract was found to contain lithium fluoride with small amounts of lithium hydroxide (5 - 10 wt %) . The LiF and LiOH content is in stoichiometric ratio to lithium consumption given in Table 1. The molar ratio of C/LiF was found to be close to 1 (for C_6F_6) or 0.43 (for C_6F_{14}) .

It is apparent that the reaction between C_6F_6 (C_6F_{14}) and lithium amalgam can be described by the equation:

$$C_6F_x + x\,Li \longrightarrow x\,(LiF) + 6\,C \quad , \; x = 6, 14 \qquad (1)$$

The elemental carbon formed is probably partly reduced by 'superstoichiometric' lithium to a compound C_yLi, which reacts with water to give lithium hydroxide:

$$C_yLi + H_2O \longrightarrow C_yH + LiOH \qquad (2)$$

This reaction is analogous to that with poly(tetrafluoroethylene) and Nafion 117, where **y** value was found to be equal to 4.8 (for PTFE) [6] or 4.9 (for Nafion 117) [20] . The **y** value in Eq. (2) is difficult to determine exactly by analysis of the water extract, and values ranging from 4 to 15 (for both reactants) were found.

Assuming **y** value ca 10, density of the C-LiF mixture 2.24 g/cm^3 [16] and diameter of the interphase 18 mm, we can calculate the average thickness of the C-LiF layer for various reaction times. The results are given in Table 2. These can be compared with the theoretical thickness of the reduction products formed on PTFE or Nafion 117 at the same experimental conditions (Table 2). It is apparent that the rate of C_6F_x ($x = 6, 14$) reduction at 25 °C is in general comparable with the reduction rate of the fluoropolymers.

TABLE 2

Calculated thickness of C-LiF product layer on various reactants at 25 °C (in μm)

Time (days)	C_6F_6	C_6F_{14}	PTFE [ref. 4,5]	Nafion 117 [ref. 20]
5	15.1	14.8	38.1	12.5
25	44.8	53.3	85.2	27.9

The mechanism of our reaction can probably again be described by an electrochemical corrosion model: The first step is a chemical reduction of C_6F_x to C-LiF mixture. In this stage, relatively long induction periods were often observed and in some cases the reaction started only on a special initiation (e.g. by high-frequency plasma discharge).The highly reactive carbon produced by this reaction starts to form a polymeric network with prevailingly sp^2 hybridized C - C bonds [9] which are the bearers of its electronic conductivity. This is one of the necessary conditions for further growing-up of the layer of reduction products; a galvanic cell with closed electrical circuit is now formed:

Li(Hg) (l) | C-LiF | C-C_6F_x (g) ,

and the reaction continues electrochemically. During the electrochemical corrosion process, electrons from the lithium anode are transported through the conductive C-LiF phase by the polymeric carbon network and reduce the C_6F_x molecules at the interphase between carbon and C_6F_x. The fluoride anions thus formed are immobile and subsequently recombine with lithium cations, which are transported from the amalgam through the C-LiF layer to the reaction site. The rate of the corrosion process is apparently controlled by the ionic conductivity of the C-LiF mixture. From this model concept it follows that the thickness of the C-LiF layer (l) can be expressed by the equation [4,5,19] :

$$\mathbf{l} = \mathbf{K} \, . \, \mathbf{t}^{1/2} \qquad (3)$$

where **t** is time and **K** is the rate constant (**K** = 58 nm.$s^{-1/2}$ for PTFE or 19 nm.$s^{-1/2}$ for Nafion 117) [4,5,20] . This is in qualitative accord with the experimental data. A quantitative evaluation of Eq. (3) would be difficult in the present case of gaseous reactants. The deviations observed (Table 2) may be due to the formation of cracks in the C-LiF layer on the liquid amalgam (mechanical shocks and temperature instability during the reaction), leading to acceleration of the reaction, but this in turn causes sealing of the cracks by the above reaction mechanism. Some deviations may also be caused by the induction period in the first stage of the process (the 'chemical stage'). The 'shaking effect' (which, of course, cannot be realized with solid polymer reactants) demonstrates that removal of the thicker, less conductive layer of C-LiF eliminates the slow transport of lithium cations through this layer and accelerates the reaction substantially.

Properties of reaction products

The X-ray diffraction patterns of our materials contain only very diffuse peaks of LiF; no signal of carbon (graphite) was detected. Using the Scherrer formula, the average size of LiF crystallites was calculated as 5.6 nm (for C_6F_6) and 4.8 nm (for C_6F_{14}). It is apparent that the product is a finely dispersed solid mixture of LiF and highly disordered polymeric carbon, modified with lithium, its structure being analogous to that of the product of PTFE reduction [16] . It is remarkable that also with simple perfluorinated hydrocarbon molecules a compact layer of solid reaction products is formed, as in the case of the polymeric PTFE chains. Apparently the carbon formed polymerises to a continuous, electronically conducting skeleton, permitting further growth by apposition from the gas phase.

X-ray photoelectron spectra of these materials contain again signals of LiF (binding energies: Li 1s 55.6 - 57.4 eV , F 1s 685.7 - 687.3 eV), but no signal of C-F bonds was detected. The C-LiF samples are strongly oxidized during a short contact with air oxygen (ca.10 minutes at room temperature), which takes place during the installation of the sample into the spectrometer. This is apparent from the signals O 1s (532.2 eV, O/C = 3.15 for C_6F_6, O/C = 0.87 for C_6F_{14}) and C1s which is a typical doublet: 285.0 and 290.0 eV , C_{290}/C_{285} = 0.94 (for C_6F_6) ; 285.1 and 289.2 eV, C_{289}/C_{285} = 0.50 (for C_6F_{14}). A similar behaviour was observed with products of fluoropolymers reduction, where the signal at higher binding energies was assigned to surface carboxyl groups [18,20] .

The principal properties of pure carbon materials (leached out with water) are summarized in Table 3.

TABLE 3

Properties of carbon materials C/benz (from C_6F_6) and C/hex (from C_6F_{14}). Samples were washed with water in contact with air and dried at 200 °C/ 1 mPa.

	C/benz	C/hex
Bulk composition	$C_{100}H_{16}O_{20}$	$C_{100}H_{19}O_{25}$
Surface composition (XPS)	$C_{100}O_{17}$	$C_{100}O_{21}$
Eb * (eV) C 1s	285.0 + 289 sh	285.0 + 289 sh
Eb * (eV) O 1s	532.8	532.7
IR bands (cm^{-1})	470 m	1100 sh
	800 w	1240 m
	1090 s	1385 m
	1150 sh	1615 s
	1380 m	1705 m
	1615 m	
	1705 m	

* Binding energy.

w = weak, m = medium, s = strong, sh = shoulder.

It is apparent that our carbons C/benz and C/hex are strongly oxidized by air oxygen. The C 1s signal in XPS is asymmetrically broadened towards higher binding energies, indicating the complicated structure of surface oxides. This is still more apparent from infrared spectra, where typical bands for C-O and C=O vibrations were detected. The infrared spectrum of C/hex is almost identical with that of the carbon prepared from PTFE [11] . The C/benz carbon differs markedly, especially by a strong peak at 1090 cm^{-1} and two peaks at 470 and 800 cm^{-1}. Our carbons contain probably various surface groups: -C-OH, -C=O, -COOH and their combinations (ethers, lactones, anhydrides, etc.), like many other carbon materials; however, their content is much higher than with other carbons, prepared by pyrolysis. This is an evidence of very high reactivity of the carbon prepared by low-temperature reduction.

The presence of hydrogen in our samples is in accord with the hydrolysis of C-LiF bonds (Eq. 2), part of the hydrogen is probably chemisorbed as surface OH or COOH groups.

CONCLUSIONS

Reaction of C_6F_x with lithium amalgam leads to an intimate mixture of LiF and elemental polymeric carbon modified with lithium, forming a compact layer which grows steadily by apposition from the gaseous reactant at the amalgam surface. The carbon is electronically conducting, highly disordered, and reactive towards oxygen; it resembles the carbon material prepared in the same way from poly(tetrafluoroethylene). The reaction of C_6F_x (x = 6, 14) with lithium amalgam proceeds via an electrochemical corrosion mechanism in which ion conduction is the rate-determining step. This mechanism seems to be generally valid for the reduction of perfluorinated materials. It is noteworthy that the quantitative splitting of C-F bonds occurs already under very mild conditions. (Some groups in the perfluorinated precursor are, on the other hand stable and remain intact in reaction with Li amalgam, like e.g. sulphonic groups in sulphonated fluoropolymers [20]). This reaction therefore presents a powerful tool for the preparation of modified carbon materials from various fluorinated starting materials and deserves further attention.

EXPERIMENTAL

Hexafluorobenzene (99 % by gas chromatography, d = 1.61 g/cm^3, T_b = 78 - 80 °C) and tetradecafluorohexane (ca.85 % of n-isomer, d = 1.684 g/cm^3, T_b =

54 - 58 °C) (both from Fluka) were distilled in vacuo, treated with Li amalgam to remove traces of humidity and oxygen, and again distilled. Liquid lithium amalgam of concentration 412 ppm by weight was used (its concentration is limited by the low solubility of Li in mercury at room temperature). The reaction was performed in an all-glass vacuum apparatus, the level of vacuum used was 1 mPa.

In a typical experiment, a precisely known amount of the amalgam (10 ± 0.5 ml) was contacted with reactant vapours at 25 °C. The vapour pressure of the reactant C_6F_x (x = 6, 14) was maintained constant during the whole experiment by equilibration with an excess of liquid C_6F_x in a side vessel (5 - 10 ml). The reaction interface C_6F_x (g) - Li(Hg) (l) was realised in an ampoule of a diameter 18.0 mm. After a chosen time of reaction, a sample of the amalgam was analysed by acidimetric titration and the consumption of lithium was calculated. The carbonaceous product was then mechanically separated from the amalgam, washed with pure mercury and finally heated to 300 °C in vacuo to remove the rest of mercury. After this procedure, the reaction vessel was opened to air and the product further investigated as follows.

X-ray diffraction patterns were obtained in the presence of air on a HZG 4A difractograph (GDR) using CuKα radiation in the transmission mode. The products were analysed on a Perkin-Elmer 240 automatic elemental analyser, the oxygen content was determined by difference. Before the analysis, the samples were washed with water to extract the LiF and dried at 200 °C / 100 mPa. The X-ray photoelectron spectra were recorded on an ESCA 3 Mk II spectrometer (VG Scientific) and evaluated using corrections for the Scofield cross-sections and kinetic energy [23,24] . The charging effect was taken into account as in ref. [18] . Infrared spectra were recorded on a Nicolet FTIR MX-1E instrument using the conventional KBr-pellet technique.

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