

X-Ray Electron Investigation of the Compounds of Fluorinated Graphite

IGOR' P. ASANOV and VERA M. PAASONEN

Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 3, Novosibirsk 630090 (Russia)

Abstract

The investigation of intercalated compounds of fluorinated graphite of the composition $C_xF \cdot yR$ was performed by X-ray electron spectroscopy. It was shown that, unlike such guest molecules as C_6H_6 , C_6F_6 , C_3H_6O , $GeCl_4$, SO_2 that interact with fluorinated graphite matrix by means of van der Waals forces, the intercalation of pyridine is accompanied by chemical interaction with the matrix resulting in the formation of fluorination products in the interlayer spaces. This causes defluorination of the matrix itself and the increase of C/F ratio. The formation of N-fluoropyridinium cations was assumed on the basis of the data obtained.

INTRODUCTION

Intercalation compounds based on fluorinated graphite (ICFGs) $C_xF \cdot yR$ are layered compounds organized as host-guest where host is the layered fluorographite matrix and guests (R) are various intercalated compounds located in the interlayer space of fluorinated graphite. ICFGs possess a series of interesting properties: high thermal and hydrolytic stability, low rate of the evolution of intercalated molecules, etc. Investigation of the host-guest interactions can be useful both for the purpose of obtaining new knowledge about the structure of intercalates and for the creation of precursors for the synthesis of new materials.

EXPERIMENTAL

In the present work we study a series of ICFGs with different intercalated molecules by means of X-ray electron spectroscopy (XES). The studies were performed with a VG Microtech spectrometer. Experimental conditions were similar to those described in [1]. Vacuum during the experiment was 10^{-8} Torr. As it was

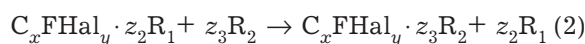
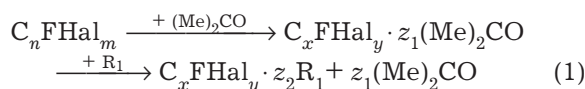
shown in [1], the bonding energy of the F 1s level in ICFGs of the $C_xF \cdot yR$ type remains constant and equal to 687.2 eV. We used this value as the reference for bond energies. The composition of surface layers was determined according to XES data using the equation for integral intensity of lines in the spectrum: $I_i \sim n_i \sigma_i \lambda_i F_i$, where n_i is the concentration of i atoms, σ_i is photoionization cross section of the inner level, λ_i is a free path of electrons. In the region of electron kinetic energy E_i investigated in the present work, electron free path was proportional to $E_i^{0.5}$; F_i is the transmittance function of the spectrometer which was determined as $\sim E_i^{-1}$ for the operation regime involved [2]. In this case we obtain that $I_i \sim n_i \sigma_i E_i^{-0.5}$. The change of atom concentration ratio obtained according to this technique using the F 1s and F 2s lines did not exceed 10 %. The programme XPSPEAK v. 4 was used to decompose spectra into the constituents.

ICFGs were synthesized according to the known technique [3] based on exchange reactions according to schemes (1), (2) with the participation of liquid intercalates (R_1 , R_2) exhibiting mutual solubility:

TABLE 1
Bond energies of the inner levels in ICFGs, eV

Intercalated molecule	C 1s	N 1s
GeCl ₄	288.8 (39 %), 286.2 (44 %), 284.8 (17 %)	–
C ₃ H ₆ O	288.6 (39 %), 286.0 (43 %), 284.9 (18 %)	–
C ₆ H ₆	288.6 (39 %), 286.0 (47 %), 284.4 (14 %)	–
C ₆ F ₆	288.6 (43 %), 286.1 (46 %), 284.8 (11 %)	–
C ₅ H ₅ N	288.6 (17 %), 288.4 (7 %), 286.7 (12 %), 285.2 (64 %)	399.1 (64 %), 401.9 (36 %)

Note. Percentage of the components in the spectra is given in parentheses.



where C_nFHal_m are ICFGs formed during the interaction of graphite with ClF_3 or BrF_3 [4, 5]; C_xFHal_y is the fluorinated graphite matrix ($x \approx 2, y \approx 0.1$ for $Hal = Cl$ and ≈ 0.02 for $Hal = Br$); R_1 and R_2 are organic reagents soluble in acetone or in each other; z_i are mole fractions of intercalantes. For the case of different R they are listed in [1].

intercalantes thus obtained were identified by means of IR, NMR spectroscopy and X-ray phase analysis. The composition of the resulting products was determined by elemental analysis. It should be noted that the intensity of absorption bands in IR spectra of ICFGs with pyridine is weak which hinders the attribution. We assume that this effect can be due to the increase of conductivity in these samples, though no measurements of such a kind were performed. The synthesis of ICFGs was described in detail in [1].

RESULTS AND DISCUSSION

Intermolecular interaction between host and guest molecules were considered in [6, 7] using NMR spectroscopy for the compounds $C_xF \cdot yR$ where R was BrF_3 , ClF_3 and C_6F_6 . The same questions were solved in [8] using X-ray fluorescent spectroscopy and XES for ICFGs with SO_2 . It was concluded on the basis of the results obtained that any noticeable interaction between the matrix and the intercalated molecules was absent.

The XES investigation of intercalation compounds based on fluorinated graphite was described in [1]. It was demonstrated using the

bond energies of the inner levels C 1s and F 1s that the contribution from ion constituent into chemical bond between carbon and fluorine atoms in the matrix of fluorinated carbon is increased, in comparison with graphite monofluoride (CF).

The parameters of X-ray electron spectra are listed in Table 1. The spectrum for C 1s is a doublet of the components of equal intensity with the energies of about 288.6 and 286.1 eV from carbon atoms of the fluorinated matrix (Fig. 1). In the region of smaller bond energies (about 284.6 eV) a small shoulder is observed. It may originate from graphite-like regions inside the fluorinated graphite matrix. It should be noted that the authors of [9] conclude from the results of modelling by means of molecular mechanics that the formation of CF regions inside the graphite matrix is energetically profitable during the fluorination of graphite. The spectrum of the F 1s level is a singlet with bond energy of 687.2 eV. Line shapes of C 1s and F 1s spectra of ICFGs with different intercalated molecules (C_6H_6 , C_6F_6 , C_3H_6O , $GeCl_4$, SO_2) remain practically the same. So, it was concluded that, in spite of different nature of intercalantes, the interaction between the matrix and intercalated molecules occurs only due to van der Waals forces but not *via* the formation of chemical bonds.

When passing from the ICFGs with the above-listed guest molecules to pyridine, the situation changes. First of all, the spectrum of the C 1s level changes (see Fig. 1). It is composed of the main component at 285 eV and a broad shoulder in higher bond energy region. The spectrum of the F 1s level is, similar to previous cases, a single line with the energy of 687.2 eV. The spectrum of N 1s level can be represented as a superposition of two components. The main component is 1.9 eV wide, its energy is 399.0 eV,

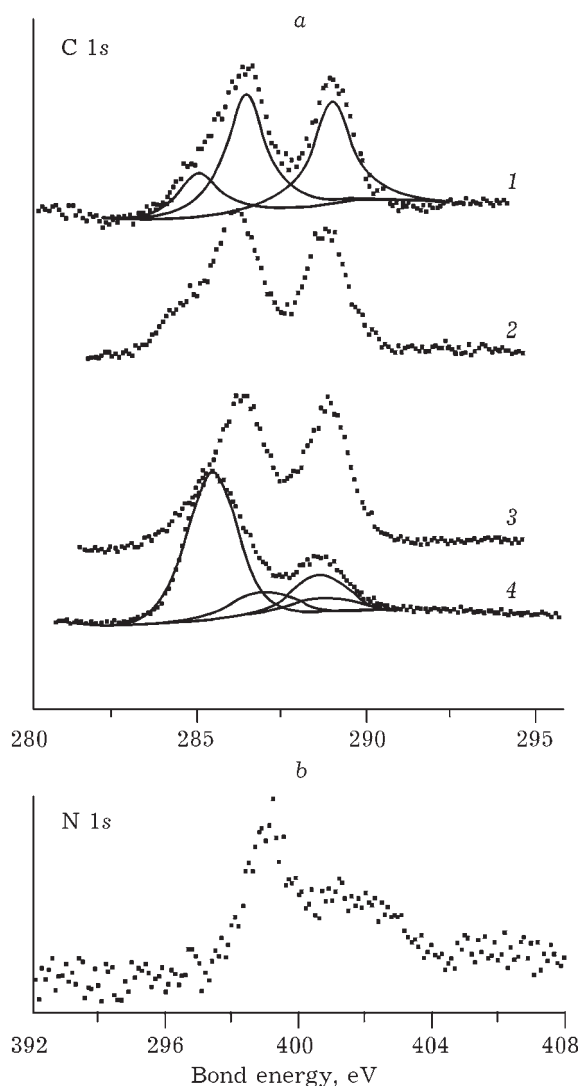
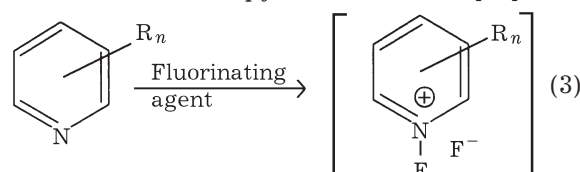


Fig. 1. X-ray electron spectroscopy of the inner levels: *a* - C 1s, ICFGs with GeCl_4 (1), C_6H_6 (2), C_6F_6 (3) and pyridine (4); *b* - N 1s, ICFGs with pyridine.

and its area is about 2/3 of the total signal. The smaller component is shifted by 2.8 eV to larger energies (see Table 1) which points to the presence of positively charged nitrogen ions. Elements ratio in the surface layer calculated according to the XES data is C : N : F = 5.6 : 0.19 : 1.

It should be noted that these results are the evidence of the changes in matrix composition, namely, of the increase in C/F ratio which was ≈ 2 for the ICFGs studied earlier (with C_6H_6 , C_6F_6 , $\text{C}_3\text{H}_6\text{O}$, GeCl_4). This fact is exhibited in the C 1s level spectrum as the increase of the line intensity at 285 eV from carbon atoms not bound to fluorine atoms. This change of the C/F ratio is likely to be the consequence of the interaction of matrix with pyridine.

In order to study the chemical bond in ICFGs with pyridine, it is important to interpret the spectrum of N 1s. The shift of the N 1s level was measured in [10] to be 2.1 eV when passing from pyridine to perfluoropyridine, which is close to the case under consideration in our paper. However, one can hardly expect complete fluorination of pyridine in fluorographite matrix under the conditions of our synthesis. On the other hand, according to [11], the difference in N 1s level energies of pyridine and monofluoropyridine in the gas phase does not exceed 0.4 eV. In order to understand the processes that occur during the interaction of intercalated pyridine with fluorographite matrix, we shall now turn to the known compounds of the $[\text{R}_3\text{NF}]^+\text{A}^-$ type in which the fluorine atom is bound to nitrogen atom. The latter gets positive charge. The data on the synthesis and fluorinating ability of N-fluoramines and their derivatives are presented in the review [12]. The fluorination of pyridine and its derivatives by fluorine or other fluorinating agents is known to lead to the formation of N-fluoropyridinium cation [13]:



Then, on the basis of our data, we can assume that between the layers of the fluorographite matrix there are both the pyridine molecules (that do not interact chemically with the matrix) and N-fluoropyridinium cations responsible for the formation of positively charged nitrogen atoms. So, the major line with the least bond energy in the N 1s spectrum (399.1 eV) is due to nitrogen atoms originating from the intercalated pyridine molecules while the line corresponding to higher energy (401.9 eV) is due to the nitrogen atoms formed in the reaction of pyridine with the fluorographite matrix.

Taking into account the data on pyridine to N-fluoropyridinium cation ratio in the matrix, as suggested by the fitting of N 1s spectrum, chemical composition of the compound can be represented by the empirical formula $\text{C}_{3.7}(\text{CF})_{0.93}(\text{C}_5\text{H}_5\text{N})_{0.12}(\text{N-fluoropyridinium})_{0.07}$. This formula depicts the ratio of the carbon atoms of graphite regions to the carbon atoms

of CF regions in fluorographite matrix, as well as the ratio of pyridine molecules to pyridinium ions in the resulting ICFGs. On the basis of these data, an attempt can be made to decompose the C 1s spectrum. In order to do this, the signal from carbon atoms of the fluorographite matrix should be represented as two components from graphite-like regions and from C—F bonds. The contributions from 4 lines of carbon in pyridine and N-fluoropyridinium should be represented as single lines with maxima in mass centres. The initial data on the bond energies of inner levels in ICFGs for fitting were taken from [1, 10]. The results of C 1s spectrum decomposition are shown in Table 1.

Literature data exhibit substantial scattering of the bond energy of N 1s level in pyridine (within the range of 398.0–400.2 eV) [14, 15], which is connected mainly with differences in energy calibration and recharge effects. Because of this, it seems impossible, in the frames of the present study, to determine chemical shift at nitrogen atom of pyridine intercalated into fluorographite matrix. Nevertheless, it should be noted that for comparison we can use the difference between the energies of inner bonds of the levels N 1s and C 1s since this difference is independent of the mentioned effects. According to the data of [10], in solid pyridine the difference between the energy of N 1s level and the energy of mass centre with respect to 4 carbon lines in the C 1s spectrum is 114.3 eV while in the case considered in the present paper the difference is 112.4 eV (399.1–286.7). This change can be the evidence of either the increased negative charge on nitrogen atom in pyridine in ICFGs or a substantial effect of the Madelung's potential on bond energies of the inner levels of pyridine in fluorographite matrix, compared to the solid state.

The parameters of C 1s spectrum (splitting between the carbon atoms of fluorographite matrix is 3.4 eV; the difference between the energies of the levels F 1s and C 1s from carbon atoms bound to fluorine atoms is 398.6 eV) indicate that the character of chemical bond between the atoms of fluorographite matrix is similar to that in other studied ICFGs [1].

As we have already mentioned, the decrease of bond energy for the component with lower

bond energy in the C 1s spectrum is connected with the increase of the area of non-fluorinated regions of the matrix. It can be noted that the C/F ratio for the matrix atoms in ICFGs with pyridine corresponds to the data concerning the appearance of conductivity, as it was mentioned above, and agrees with the results reported in [16]. However, unlike the data of the latter work, C—F chemical bond is not completely ionic in the concentration range under consideration.

Of course, in order to confirm the assumption concerning the formation of N-fluoropyridinium cation, additional investigations are required. However, at the present stage the XES data suggest that the fluorographite matrix which is indifferent to various guest molecules, for example the above-mentioned C_6H_6 , C_6F_6 , C_3H_6O , $GeCl_4$, etc. interacts with pyridine, which results in the formation of fluorination products in the interlayer galleries. In turn, this leads to defluorination of the matrix itself and to the increase of C/F ratio. In particular, one of the evidences is the fact that the fraction of carbon atoms from graphite regions increases to 60 %. It is remarkable that this effect is large, since the fraction of fluorine atoms from N-fluoropyridinium cations is only 7 % of their total number.

This is one of the reasons why the F 1s spectrum is a single non-shifted line. Earlier it was noted that fluorographite matrix interacts with the intercalated compound during thermal action. For example, it was shown in [17, 18] that the interaction of the matrix with such guest molecules as SO_2 , $GeCl_4$ leads to the formation of a complex mixture of gaseous products and carbon phase at $T \sim 480\text{--}590$ K which is substantially below the temperatures at which thermal decomposition of "high-temperature" fluorinated graphite is observed [19]. These facts were explained by the so-called semi-ionic character of the C—F bond which possesses less energy than the covalent C—F bonds in fluorinated graphite obtained in the system fluorine – graphite at increased temperatures. In the case of pyridine, the interaction with semi-ionic C—F bonds takes place at room temperature.

CONCLUSION

The investigation of ICFGs with pyridine was performed by means of XES. It was stated that chemical interaction of pyridine molecules with the fluorographite matrix occurs during intercalation. On the basis of the data obtained, it was assumed that N-fluoropyridinium cation is formed. The results of the study can be useful from the viewpoint of the search for new fluorinating reagents and investigation of chemical processes in microreactors based on C_xF .

REFERENCES

- 1 I. P. Asanov, V. M. Paasonen, L. N. Mazalov and A. S. Nazarov, *Zhurn. struktur. khimii*, 39 (1998) 1127.
- 2 V. I. Nefedov and V. T. Cherepin, *Fizicheskiye metody issledovaniya poverkhnosti tverdykh tel*, Nauka, Moscow, 1983.
- 3 N. F. Yudanov, A. S. Nazarov and I. I. Yakovlev, *Tez. VI Vsesoyuz. simpoz. po khimii neorganicheskikh ftoridov*, Novosibirsk, 1981, p. 94.
- 4 A. S. Nazarov, V. G. Makotchenko and I. I. Yakovlev, *Zhurn. neorgan. khimii*, 23 (1978) 1680.
- 5 Yu. I. Nikonorov and L. L. Gornostayev, *Izv. SO AN SSSR. Ser. khim. nauk*, 9 (1979) 55.
- 6 A. M. Panich, A. N. Danilenko, A. S. Nazarov *et al.*, *Zhurn. struktur. khimii*, 26 (1988) 3269.
- 7 S. P. Gabuda, S. G. Kozlova, V. M. Paasonen and A. S. Nazarov, *Ibid.*, 41 (2000) 80.
- 8 V. M. Paasonen, S. B. Erenburg, A. S. Nazarov *et al.*, *Ibid.*, 38 (1998) 350.
- 9 N. N. Breslavskaya, P. N. D'yachkov and E. G. Ippolitov, *Dokl. AN*, 325 (1992) 751.
- 10 D. T. Clark, R. D. Chambers, D. Killkast and W. K. R. Musgrave, *J. Chem. Soc. Faraday Trans. II*, 68 (1972) 309.
- 11 R. Brown and A. Tse, *Canad. J. Chem.*, 58 (1980) 694.
- 12 G. G. Furin, in L. German and S. Zemskov (Eds.), *New Fluorinating Agents in Organic Synthesis*, Springer-Verlag, Berlin, 1989, p. 34.
- 13 T. Umemoto and K. Tomita, *Tetrahedron Lett.*, 27 (1986) 3271.
- 14 V. I. Nefedov, *Rentgenoelektronnaya spektroskopiya khimicheskikh soyedineniy: Reference book*, Nauka, Moscow, 1984.
- 15 L. N. Mazalov and V. D. Yumatov, *Elektronnoye stroyniye ekstragentov*, Nauka, Novosibirsk, 1984.
- 16 A. M. Panich, T. Nakajima and S. D. Goren, *Chem. Phys. Lett.*, 271 (1997) 381.
- 17 V. M. Paasonen, A. S. Nazarov, V. M. Grankin and I. I. Yakovlev, *Zhurn. neorgan. khimii*, 35 (1990) 2205.
- 18 V. M. Paasonen, V. M. Grankin and A. S. Nazarov, *Neorgan. materialy*, 35 (1999) 179.
- 19 P. Kamarchik and J. L. Margrove, *Acc. Chem. Res.*, 11 (1978) 296.