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On the Possible Use of Dicarbon Fluoride Intercalates as Containers for Volatile Substances

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Abstract

A possibility has been shown to create molecular chemical containers for the storage, the transportation and release in the environment of gaseous and liquid, chemically and physiologically active materials on the basis of a matrix of dicarbon fluoride. As regards a set of operational parameters such as the versatility in respect to the introduced material (*i.e.* capacity to form compounds with various classes of inorganic and organic matters), the thermal (up to 390 °C) and hydrolytic stability, capacity (up to 30 mass %), the protection degree of the introduced material against the influence of external factors and the storage period (for years), the new molecular chemical containers on the basis of dicarbon fluoride outperform the containers on the basis of alternative familiar types of inclusion compounds.

INTRODUCTION

To decrease or eliminate the fugitiveness, the toxicity, to reduce the fire or explosion hazard, to enhance the protection from the external medium, to supply convenient forms for a dosage or operation, *etc.* of volatile matters, various methods of their containerizing are considered in the literature. Accordingly, in early '70s of the past century, the application of microencapsulation tech-niques for these purposes [1] was widely discussed. A great attention is also being given to sorbent technologies. On the 11th International symposium on inclusion compounds, a significant part of the works has been devoted to methods of obtaining expanded graphite from graphite intercalates and to its sorption properties [2]. A much less frequent use for containerizing volatile matters is made of inclusion compounds [3, 4]. Their widespread application as volatile matters is hindered, primarily, by a high pressure of decomposition of these compounds and by a low versatility (the capacity to form inclusion compounds) in relation to an introduced material. The versatili-ty is limited by the fact that a favourable relation of "host" and "guest" molecular geometries is essential to form the inclusion compounds of cellular or channel types [4].

At the same time, analysis of literary data on crystal chemistry of inclusion compounds allows an assumption that creating new effective molecular containers is possible on the basis of the inclusion compounds that are constructed by the host-guest principle. It is obvious that with the van der Waals nature of the interaction in a host-guest system, the guest molecules retain their intrinsic chemical and physiological properties and in doing so, they provide the main functional purpose of the container. In a physicochemical aspect, the inclusion compounds are homogeneous systems, that is, they constitute molecular chemical containers (MCC) in their essence.

"Guest" molecule within the structures of inclusion compounds cannot be strongly held in the "host" structure, if it has an insufficient strength. Therefore, in order that steady clathrates are formed, the components of the cell itself must be strongly linked among themselves by chemical (ionic or covalent) bonds. If there is a cellular structure around the incorporated molecule and the structure is formed due to ionic or covalent bonds, then an energy barrier of the internal stress in the host-guest system must be sufficiently high and it will be determined by the energy of the chemical bond between the components of the "host". Therefore, to "release" the trapped molecule, it is necessary to destroy a cell of the "host", having disrupted the chemical bonds between its components. Consequently, if these clathrate compounds have been formed, they will be hardly amenable to decomposition. However, obtaining this type of compounds in practice involves difficulties.

From this point of view, layered structures, in particular graphite, are the most promising. In graphite, the interaction in the host–guest system is of an elastic nature, *i.e.* an introduced molecule itself moves the graphite layers apart and shapes a hollow according to its size. Therefore, the size and geometry of the "guest" molecule in this case are not the factors that limit the formation of layered graphite compounds. Second, graphite possesses a sufficiently high chemical inertness that makes it possible to incorporate sufficiently strong reducers or oxidizers in its structure, which is followed by the formation of the associated intercalated compounds of graphite [5]. However, graphite, along with alternative layered structures, possesses a low versatility with respect to the introduced material. Accordingly, graphite is capable to form the layered compounds only with the substances that feature donor or acceptor properties [5]. To put it another way, in order to form the layered compounds of graphite, a transfer of an electron is required either from a "guest" molecule onto the carbon atoms of the graphite layers, or from carbon on the "guest" molecule. In addition, layered compounds of graphite show a high pressure of decomposition and a low protection degree of the "guest" from the influence of external factors, which makes the graphite matrix to be of little promise for creating molecular chemical containers on its basis.

It is obvious that if the graphite interlayer gaps are partitioned across (are closed) by atoms or functional groups that are chemically linked by ionic or covalent bonds with the carbon atoms of the graphite lattice orthogonally to its plane, then the formation of new structures is possible that hinder the free release of an intercalated "guest" molecule. It is also possible to expect that a "shielding" of the graphite structure by atoms or functional groups will change an intercalation capacity of these modified graphites (a capacity to form layered compounds). These compounds are exemplified by oxidized compounds of graphite, namely, monocarbon polyfluoride $(CF)_n$ [6], tetracarbon polyfluoride $(C_4F)_n$ [7] and graphite oxides [8] that are familiar from literary data.

One of the examples of the oxidized graphite is dicarbon polyfluoride being formed through the interaction of graphite with strong fluoroxidizers according to the scheme

$$\text{graphite} + EF_n \rightarrow C_2F \cdot xEF_n + R \quad (1)$$

where EF_n is a fluoroxidizer, R is a reduced form of the fluoroxidizer.

As can be seen from Table 1, the nature of the applied fluoroxidizer (chlorine trifluoride, chlorine pentafluoride, xenon difluoride), the synthesis method (a gaseous or liquid phase) and temperature, introduction of solvent into the reaction (anhydrous fluorine hydride or trichloro-trifluoroethane) have no effect on the graphite fluorination degree. Dicarbon polyfluoride with the atomic ratio $C/F \approx 2$ is formed in all cases, this polyfluoride being in the form of its intercalated compounds akin to $C_2F \cdot xEF_n$ or $C_2F{\cdot}xEF_n \cdot x_1R$, where EF_n is a fluoroxidizer molecule, R is a solvent molecule.

Characteristic feature of intercalated compounds of dicarbon fluoride with the fluoroxidizers that were produced under the scheme 1 is their interaction with certain reagents R (dinitrogen tetroxide [9], acetone [10], acetonitrile [11], anhydrous nitric acid [12] and cyclohexanone) to form intercalated compounds of dicarbon fluoride with the corresponding intercalants of the first stage of the filling (1). This allows conducting the reactions of replacement of certain intercalants (R) by the others (R_1)

TABLE 1

Influence of the synthesis method and conditions on the graphite fluorination degree

Synthesis	T, °C	Size of graphite particles, μm	Empirical formula
$C + ClF_{3,l}$	20	–	$C_2F_{0.90}Cl_{0.06} \cdot 0.13ClF_3$
$C + XeF_2 + HF$	20	–	$C_2F_{0.88}. \cdot n_1XeF_2 \cdot n_2HF$
$C + XeF_2 + HF$	40	–	$C_2F_{0.93} \cdot n_1XeF_2 \cdot n_2HF$
$C + XeF_2 + HF$	90	–	$C_2F_{0.94} \cdot n_1XeF_2 \cdot n_2HF$
$C + ClF_{5,l}$	20	–	$C_2FCl_{0.03} \cdot n_1ClF_5 \cdot n_2ClF_3$
$C + ClF_3 + C_2F_3Cl_3$	20	–	$C_2F_{0.93}Cl_{0.06} \cdot n_1ClF_3 \cdot n_2C_2F_3Cl_3$
$C + ClF_3 + HF$ 82.1 : 17.9	20	–	$C_2F_{0.91}Cl_{0.07} \cdot n_1ClF_3 \cdot n_2HF \cdot n_3ClO_2$*
$C + ClF_3 + HF$ 59.7 : 40.3	20	–	$C_2F_{0.91}Cl_{0.09} \cdot n_1ClF_3 \cdot n_2HF \cdot n_3ClO_2$*
$C + ClF_3+HF$ 33.6 : 66.4	20	–	$C_2F_{0.92}Cl_{0.09} \cdot n_1ClF_3 \cdot n_2HF \cdot n_3ClO_2$*
$C + ClF_3 + HF$ 7.1 : 92.9	20	–	$C_2F_{0.91}Cl_{0.08} \cdot n_1ClF_3 \cdot n_2HF \cdot n_3ClO_2$*
$C + ClF_{3,l}$	20	10	$C_2F_{0.92}Cl_{0.07} \cdot 0.12ClF_3$
$C + ClF_{3,l}$	20	≤100	$C_2F_{0.92}Cl_{0.08} \cdot 0.13ClF_3$
$C + ClF_{3,l}$	20	≤200	$C_2F_{0.91}Cl_{0.08} \cdot 0.13ClF_3$
$C + ClF_{3,l}$	20	≤400	$C_2F_{0.90}Cl_{0.07} \cdot 0.12ClF_3$
$C + ClF_{3,l}$	20	≥400	$C_2F_{0.92}Cl_{0.07} \cdot 0.12ClF_3$
$C + ClF_{3,g}$	50	–	$C_2F_{0.91}Cl_{0.05} \cdot 0.13ClF_3$
$C + ClF_{3,g}$	100	–	$C_2F_{0.93}Cl_{0.04} \cdot 0.13ClF_3$
$C + ClF_{3,g} + HF_g$	20	–	$C_2F_{0.90}Cl_{0.06} \cdot n_1ClF_3 \cdot n_2HF$
$C + ClF_{3,g} + HF_g$	100	–	$C_2F_{0.93}Cl_{0.06} \cdot n_1ClF_3 \cdot n_2HF$

*ClO_2 is formed as a result of ClF_3 interaction with water that is brought in with fluorine hydride [19].

and also by solutions. Upon removing of an excess of the liquid phase R or R_1, intercalated compounds of the first stage of the filling transform to the compounds of the second stage, *i.e.* carrying out the consecutive replacement reactions is possible in compliance with the schemes

$$C_2F \cdot xEF_n + R \rightarrow C_2F \cdot x_1R + \text{products of interaction of } EF_n \text{ and } R \quad (2)$$

$$C_2F \cdot x_1R + R_1 \rightarrow C_2F \cdot x_2R_1 + R \quad (3)$$

Table 2 presents the examples of the intercalated compounds of dicarbon fluoride with certain organic and organic intercalants that were obtained in accordance with the schemes (2) and (3). It is evident that carrying out the consecutive replacement reactions makes possible a purpose-oriented replacement of a fluoroxidizer in the intercalated compounds obtained under the scheme (1) by practically any other organic or inorganic substance, the boiling point of which is within the range from −150 to +240 °C. As opposed to graphite that forms intercalated compounds only with the substances that show donor-acceptor properties, the formation of intercalated compounds around dicarbon fluoride akin to $C_2F \cdot xR$ is not limited by this factor. This is related to the fact that the host-guest interaction in the intercalated compounds of this type is of a van der Waals nature. It should be also noted that the matrix of dicarbon fluoride retains the layered structure that is inherent in graphite (Fig. 1). As a consequence, the size and geometry of a molecule intercalating in the structure of dicarbon fluoride, as is the case with graphite, are not the factors that limit the formation of intercalated compounds. Intercalation of the compounds, which are crystalline under normal conditions, into dicarbon fluoride in the form of their solutions in the associated non-aqueous solvents is possible too. By virtue of the fact

TABLE 2

Examples of the intercalated compounds of dicarbon fluoride with inorganic and organic matters

Intercalant (R)	Boiling point, °C	Content, mass %	Decomposition temperature, °C
N_2O_4	21	22.3	120
HNO_3	83	20.2	130
C_5H_{12}	36	10.3	140
C_7H_{16}	93	11.1	140
CCl_3F	24	20.4	390
CCl_4	77	22.7	390
$(CH_3)_2CO$	56.2	13.8	120
CH_3OH	64.7	12.5	120
C_2H_5OH	78.3	13.8	120
iso-C_3H_7OH	97	12.2	130
n-$C_8H_{17}OH$	194.5	9.6	140
$CH_3COOC_4H_9$	126	14.0	140
C_6H_6	80.1	15.2	150
$C_6H_5CH_3$	110.6	15.6	140
o-$C_6H_4(CH_3)_2$	144.4	15.9	140

that carbon atoms in dicarbon fluoride “are screened” by the attached fluorine atoms, the formation of intercalated compounds is conceivable even with such strong oxidizers as nitric acid, halogen fluorides, *etc.*

Intercalated compounds of dicarbon fluoride similar to $C_2F \cdot xR$ fall into host-guest systems, wherein the “guest” molecules are arranged in the form of monomolecular liquid-like layers between the fluorinated carbon layers that make up a crystal structure of a dicarbon fluoride matrix. The processes of an intercalation into the layered matrices differ from the sorption processes first of all by the fact that their efficiency is determined not by the macroscopic properties of the matrix (the specific surface, the pore or capillary size, the functional groups existing on the surface, *etc.*), but by its crystal structure and by the nature of intermolecular interactions between the layers of an intercalant (an introduced material) and the layers of the matrix. This difference is obviously shown by a distinction in the sorption and intercalation properties of oxidized graphite. Although a specific surface of oxidized graphite, in particular dicarbon fluoride, is small (several square meters per gram), the content of the oxidized substance in oxidized graphites can range up to 30 mass %.

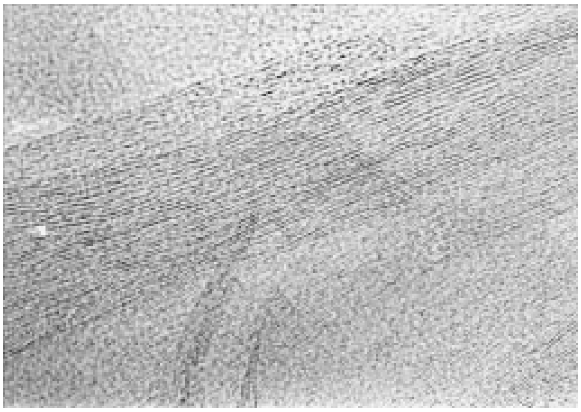

Fig. 1. Electronic microdiffraction pattern for an intercalated compound of dicarbon fluoride with chlorine trifluoride of the second stage.

As can be seen from Table 2, thermal stability of intercalated compounds of dicarbon fluoride of the second stage is rather high and it varies in the region of values 120–390 °C depending on the chemical properties of the intercalant. In addition to their high thermal stability, intercalated compounds of dicarbon fluoride of the second stage show a low pressure of decomposition even in the case when the compounds with boiling point from −100 to

−150 °C are introduced as a "guest". Because of the fluorine incorporated into the graphite structure, the matrix of dicarbon fluoride becomes hydrophobic and it is distinguished from other matrices of oxidized graphite in a high protection degree of the "guest" molecule against an influence of external factors (a moisture, an air oxygen, *etc*.). Therefore, intercalated compounds of dicarbon fluoride of the second stage can be stored in the air medium for a long time (for years) practically without any appreciable change in their composition.

As regards the properties specified (a low pressure of decomposition, a high thermal and hydrolytic stability), the intercalated compounds of dicarbon fluoride of the second stage significantly differ both from the intercalated compounds of graphite and from the associated intercalated compounds of the first stage of the filling. Accordingly, the latter are stable only under a layer of the liquid phase of an intercalant [10, 13], while the intercalation energy of the substance differs from its enthalpy of evaporation by 1−2 kcal/mol [11]. The fact of the elevated stability of the intercalated compounds of dicarbon fluoride of the second stage is still waiting for an explanation.

Nevertheless, in the case that fluorine atoms from graphite fluorides have a dipole moment [14, 15], it can be inferred that their mutual repulsion will occur due to the dipole-dipole interaction of the like-charged end atoms of fluorine of the unfilled layers. In consequence of this, the terminal sites of the fluorinated graphite layers must occupy an averaged position with an identical interlayer distance. Thus, it is probably the dipole-dipole interaction of the end fluorine atoms of the unfilled layers that ensures an effective "lock-out" of the intercalated "guest" molecules between the layers of dicarbon fluoride. Indeed, to deintercalate the introduced molecule in this case, it is necessary that the molecule move apart the matrix layers, i.e. the kinetic energy of the molecule has to be over the dipole-dipole energy of the end fluorine atoms. In the compounds of the first stage of the filling, the end fluorine atoms of fluorographite layers are separated by layers of an intercalant and consequently the dipole-dipole interaction must be lacking, since it decreases proportionately to the r^3 magnitude and it cannot block a free deintercalating of the introduced molecules.

This assumption was also verified by HREM data for intercalated compounds of dicarbon fluoride (see Fig. 1). It is evident that the distance between the layers is identical and it comprises approximately 7.8 E. This value is approximately 2 times less than an identity period for a compound of dicarbon fluoride with chlorine trifluoride of the second stage [13].

Mass spectrometry data testify to a possibility for the intercalated compounds of dicarbon fluoride of the second stage similar to $C_2F \cdot xR$ to function as molecular chemical containers. The mass spectra of intercalated compounds of dicarbon fluoride with dinitrogen tetroxide (Fig. 2) [16] and benzene (Fig. 3) of the second stage are examples.

As can be seen from Fig. 2, the emergence of gaseous products upon heating the intercalated compound of dicarbon fluoride with dinitrogen tetroxide of the second stage is evidenced at 100 °C. Over the region of 100−190 °C, only the peaks of the NO_2^+, NO^+, O^+ and N^+ ions are detected. A correlation of the comparative intensity of these ions with the data [17] on the mass spectra of dinitrogen tetroxide testifies that a single gaseous product of thermal decomposition of the intercalated compound of dicarbon fluoride with dinitrogen tetroxide of the second stage in this temperature range is nitrogen dioxide arising upon a dissociation of dinitrogen tetroxide. At the temperatures over 190 °C, CO_2^+ ions appear in the mass spectrum along with the nitrogen dioxide ions, which bears witness to the chemical interaction of the intercalated dinitrogen tetroxide with the fluorographite matrix. Thus, mass spectrometry data allow a conclusion that dicarbon fluoride represents an effective molecular chemical container of dinitrogen tetroxide, the container being capable of its complete release into a gas phase in the temperature range of 100−190 °C.

A comparison of the mass spectrum for thermal decomposition of the intercalated compound of dicarbon fluoride with benzene of the second stage (see Fig. 3) with literary data on the benzene mass spectrum [18] demostrates that in a temperature range of 100−150 °C, benzene is the main product in gas evolution.

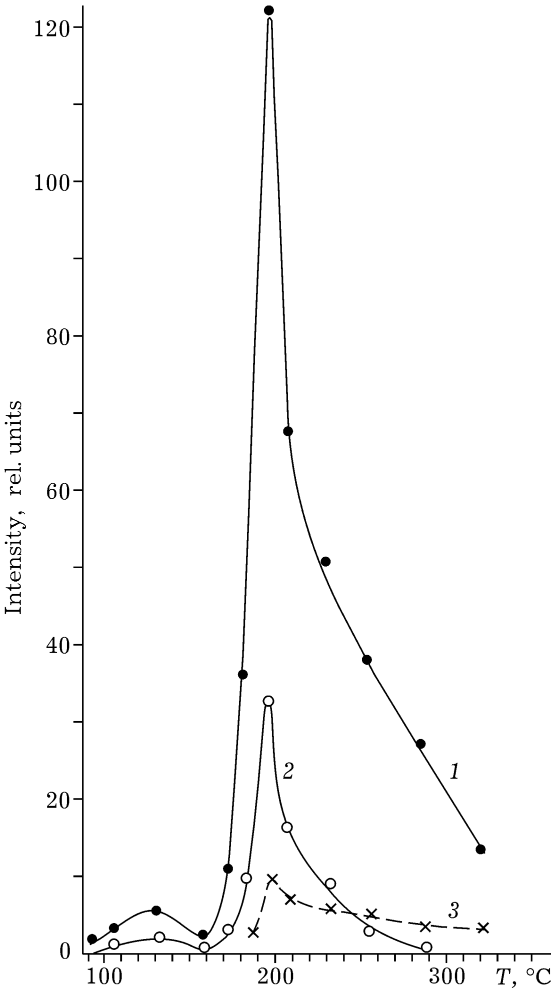

Fig. 2. Mass spectrum of gaseous products of thermal decomposition for an intercalated compound of dicarbon fluoride with dinitrogen tetroxide: *1* – NO$^+$ (30 *m/e*), *2* – NO$_2^+$ (40 *m/e*), *3* – CO$_2^+$ (44 *m/e*).

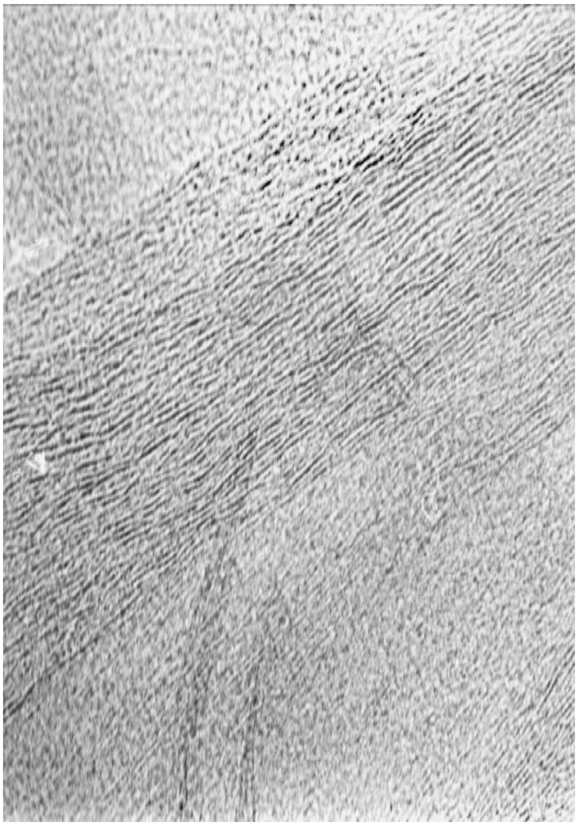

Fig. 3. Mass spectrum of gaseous products of decomposition for an intercalated compound of dicarbon fluoride with benzene at 150 °C.

Intensity of other peaks that can be interpreted as ionic peaks of the products of the interaction of dicarbon fluoride with the intercalated benzene at the temperatures as great as 150 °C does not exceed the tenth fractions of percent.

CONCLUSIONS

As it was mentioned above, an interaction in a host-guest system in intercalated compounds of dicarbon fluoride is of a van der Waals nature. Therefore, intercalated molecules retain their intrinsic chemical and physiological properties. That is the reason that the intercalated compounds of dicarbon fluoride are molecular chemical containers in their essence. Results of the research of chemical and physicochemical properties of intercalated compounds of dicarbon fluoride allow the following conclusion. As regards a set of operational parameters such as the capacity (up to 30 mass %), the thermal (100–390 °C) and hydrolytic stability, the resistance against an influence of external factors (a moisture, air oxygen, sunshine, *etc.*), the storage period (for years), the versatility in relation to the introduced substance, these compounds outperform alternative types of inclusion compounds.

Thus, an intercalation of volatile matters in a dicarbon fluoride matrix allows the most versatile solving the problem of molecular containerizing of cryogenic and liquid substances with the aim of their storage, transportation and use in a “pseudo-solid” state.

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