Thermal Decomposition of Palladium Acetylacetonate Intercalated into Dicarbon Fluoride

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Abstract

Thermal decomposition of palladium acetylacetonate intercalated into fluorocarbon matrix is investigated by means of mass spectrometry. It is demonstrated that thermal decomposition occurs within a narrower temperature range, at higher rate and comes to its completion at lower temperature (~200 °C) than for the case of individual $Pd(AA)_2$.
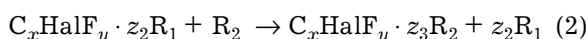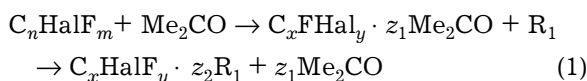
INTRODUCTION

Intercalation compounds of fluorinated graphite (FG) of the $C_2F \cdot yR$ type are layered inclusion compounds organized according to the guest – host principle, the role of a host being played by the fluorographite matrix (FG matrix), while guests (R) are the molecules of various inorganic, organic compounds or their solutions in anhydrous solvents [1–3]. Intercalated molecules occur in the interlayer space of the FG in the form of unimolecular layers with high molecular dynamics [4, 5] which is conserved till very low temperature (−100 ... −120 °C). The presence of fluorine atoms, which are strongly bound (by chemical bonds) to the carbon atoms with coaxial orientation with respect to the graphite layers of the FG matrix, can pose spatial limitations on the region in which reactions can occur in the interlayer space of the FG. This must bring about the conditions similar to those occurring in some known microreactors, for example Langmuir – Blodgett films [6]. The reactivity, mechanism and rates of chemical reactions are known to be able to change in micro reactors [7]. Because of the above considerations, one may expect the change in reactivity and, first of all, in thermal stability of a guest when chemical reac-

tions are performed in the interlayer space of FG under the conditions of two-dimensional state of intercalant.

In the present work, we investigated thermal decomposition of palladium acetylacetonate $Pd(AA)_2$ intercalated into FG in the form of the solution in chloroform. The choice of this object as a model intercalant was explained by the fact that volatility of palladium β-diketonates, their thermal stability in the condensed and gas-phase states, character of thermal decomposition, effect of reductive and oxidative media on thermal decomposition in the gas medium have been well investigated by present [8, 9].

EXPERIMENTAL

We investigated FG intercalates in which guest molecules (chloroform or $Pd(AA)_2$ solution in chloroform) occupy the space between the layers of FG. Known procedures based on exchange reactions were used to synthesize the intercalates [1, 2]:

$$C_nHalF_m + Me_2CO \rightarrow C_xFHal_y \cdot z_1Me_2CO + R_1$$
$$\rightarrow C_xHalF_y \cdot z_2R_1 + z_1Me_2CO \quad (1)$$

$$C_xHalF_y \cdot z_2R_1 + R_2 \rightarrow C_xHalF_y \cdot z_3R_2 + z_2R_1 \quad (2)$$

where C_nHalF_m is the FG intercalate formed in the interaction of graphite with ClF_3 [10] or BrF_3 [11], C_xHalF_y is the FG matrix, x value is close to 2, y is close to 0.1 for Hal = Cl and to 0.02 for Hal = Br, R_1 is $CHCl_3$, R_2 is the solution of $Pd(AA)_2$ in $CHCl_3$. The $Pd(AA)_2$ was synthesized according to [8].

In order to confirm the identity of $Pd(AA)_2$, we performed mass spectrometric and IR spectroscopic investigations. Mass spectrometric data that characterize the composition of the main gas-phase products of the synthesized $Pd(AA)_2$ correspond to the literature data [9]. IR spectra of the complex are identical with those reported in [12], which is another confirmation of the identity of the complex. The intercalates obtained according to schemes (1) and (2) were investigated by means of XPA, IR spectroscopy, and mass spectrometry.

IR spectra in the region of $3800-400$ cm^{-1} were recorded with Specord-75 IR spectrophotometer (tablets with KBr). X-ray diffraction patterns were recorded with DRON-3M diffractometer (CuK_α radiation, Ni filter). Samples under a layer of liquid phase were recorded using a cell made of fluoroplastics, closed with a fluoroplastic film 5 μm thick. The dried samples were recorded using a standard quartz cell with preliminarily deposited vacuum grease. The composition of gas-phase products evolved during the heating of intercalate was established by means of mass spectrometry. Mass spectra were recorded with MI-1201 mass spectrometer. A sample (4–5 mg) was placed into Knudsen's effusion chamber made of nickel. The temperature of the chamber was varied stepwise with an arbitrary step; at each established temperature, full mass spectrum of the formed products was recorded during the required time interval.

RESULTS AND DISCUSSION

X-ray diffraction patterns of the intercalate samples with $CHCl_3$ or with the solutions of $Pd(AA)_2$ in $CHCl_3$ (recorded under a layer of solvent or solution) are characterized by the presence of $00l$ reflections corresponding to the interlayer distance of the corresponding intercalate of the first stage of filling (n_1).
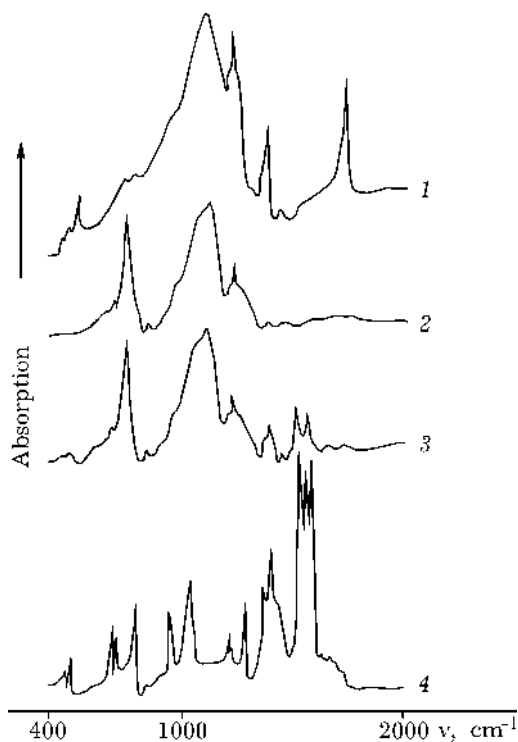

Fig. 1. IR spectra of intercalates with acetone (*1*), chloroform (*2*) and solution of $Pd(AA)_2$ in chloroform (*3*), as well as the spectrum of the individual complex $Pd(AA)_2$ (*4*).

The d_{001} and d_{002} reflections were 10.20 and 5.10 Å, respectively, both for the intercalate with $Pd(AA)_2$ solution in $CHCl_3$ (R_3) and for the intercalate (R_2)*. In other words, in the case of intercalation of $Pd(AA)_2$ solution, the thickness of the filled layer of intercalate, which is a sum of the interlayer space in the FG matrix (6.1 Å for C_nClF_m [13] and 6.0 Å for C_nBrF_m [1]) and the thickness of the layer of guest, is determined by the molecular size of solvent ($CHCl_3$), which in turn is the evidence of parallel orientation of the plane of $Pd(AA)_2$ complex with respect to the FG matrix. Diffraction patterns of intercalates with R_2 and R_3 dried in the air are characterized by the presence of strongly broadened reflections; their observed positions (8.00 and 5.37 Å) allow assigning them to the 002 and 003 reflections of intercalates n_2 with the identity period ~16 Å. It should be noted that the reflections $00l$ corresponding to stage n_1 are observed in the diffraction patterns of

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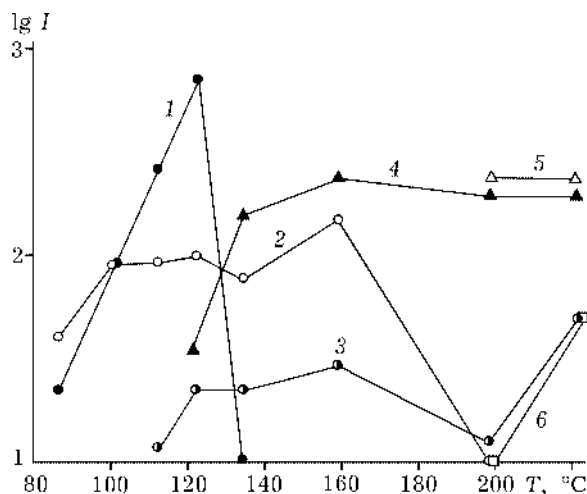*Reflection values are given for intercalated synthesized using C_nBrF_m.

Fig. 2. Temperature dependence of the intensity of ion peaks of the main gas-phase products at the initial step of thermolysis of the intercalate with Pd(AA)$_2$: 1 – Pd(AA)$_2$, 2 – HAA, 3 – CHCl$_3$, 4 – HF, 5 – CFCl$_2$, 6 – CF$_2$Cl$_2$.

n_2 intercalates, similarly to the case of previously investigated ones [14].

IR absorption spectra of intercalates obtained consequently according to schemes (1) and (2) with acetone, chloroform and Pd(AA)$_2$ solution in chloroform, as well as the spectrum of Pd(AA)$_2$ complex, are shown in Fig. 1. The spectra of all the intercalates under consideration contain absorption bands (1100–1200 cm^{-1}) of C–F bond

in FG, as well as intercalants: acetone (1715, 1360, 1220, 533 cm^{-1}), chloroform (1210, 750 cm^{-1}), and Pd(AA)$_2$ solution in chloroform (1570, 1520, 1395, 1210, 750 cm^{-1}) and the most intensive absorption bands of Pd(AA)$_2$ (1100–1200 cm^{-1}). Due to insignificant content of the complex in the intercalate, the absorption bands of the complex in the region of 1270–937 cm^{-1} are overlapped by more intensive absorption bands of C–F bond and chloroform; in the region of 790–660 cm^{-1}, they are overlapped by an intensive absorption band of chloroform.

So, according to the data of IR spectroscopy and XPA, the introduction of Pd(AA)$_2$ into FG as a solution in chloroform in consistency with schemes (1) and (2) leads to obtaining the corresponding intercalate.

Experimental results of the investigation of thermal decomposition of intercalate with Pd(AA)$_2$ are shown in Figs. 2–4. According to the data of mass spectrometry, the start of emission of products is observed at the temperature of 87 °C. The products include molecular ions Pd(AA)$_2$, fragmental metal-containing ions, as well as the ions of free ligand HAA and its fragmental ions. At 112 °C, CHCl$_2$ radicals start to evolve; at $T > 122$ °C, HF molecules are released. It is typical that in the latter case the
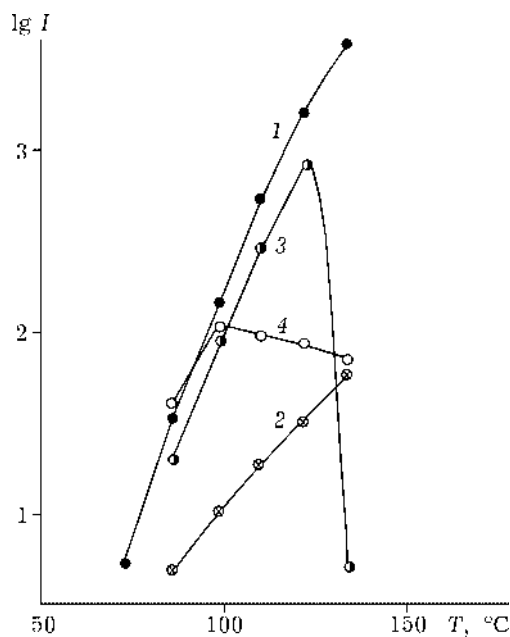

Fig. 3. Temperature dependence of the intensity of ion peaks of Pd(AA)$_2$ and HAA on heating individual complex ($1, 2$) and its intercalate ($3, 4$).
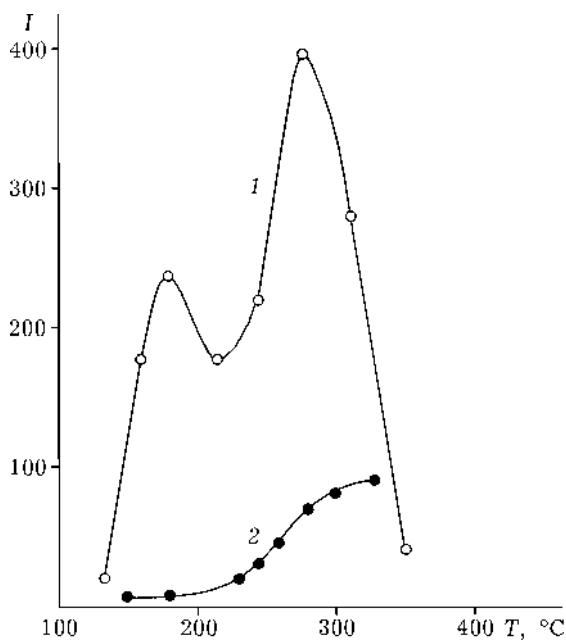

Fig. 4. Temperature dependence of HF liberation on heating intercalate with Pd(AA)$_2$ in CHCl$_3$ solution (1) and intercalate with CHCl$_3$ (2).

m/z	Ion	Content, %
31	$[CF]^+$	25.7
47	$[CCl]^+$	26.1
50	$[CF_2]^+$	7.1
66	$[CFCl]^+$	30.0
69	$[CF_3]^+$	21.4
85	$[CF_2Cl]^+$	38.6
101	$[CFCl_2]^+$	100

amount of complex in the gas phase decreases sharply (to zero), in other words, no metal-containing fragments are observed in the mass spectra at $T > 122$ °C, while HAA goes on being evolved till 200 °C. At temperature above 200 °C, HAA is absent from mass spectra; we observe only chlorofluorocarbons ($CFCl_2$, CF_2Cl), HF, $CHCl_2$, as well as COF_3, COF, CF_2COH. On further temperature increase, radical products appear: $CFCl_3$ ($T > 250$ °C), C_2Cl_4 ($T > 280$ °C) and HCl ($T > 300$ °C). At temperature above 330 °C, the decomposition of fluorographite matrix starts, which is confirmed by the presence of fluorocarbon ions in the mass spectra (Table 1). These ions are characteristic of thermal destruction of FG matrix [13, 15]. The initial stage of thermal decomposition of the intercalate with $Pd(AA)_2$ is shown in Fig. 2; Fig. 3 shows temperature dependence of the intensity of ion current of molecular $Pd(AA)_2$ and the free ligand HAA for the individual $Pd(AA)_2$ complex (curves *1, 2*) and for its intercalate (curves *3, 4*).

It was demonstrated previously in the investigation of thermal stability and temperature dependence of $Pd(AA)_2$ vapour pressure [9] that within the temperature range of 86–138 °C the complexes in the solid state are slowly decomposed evolving HAA molecules; according to DTA data, the decomposition in helium starts at $T > 200$ °C. Gas-phase complexes in vacuum start to decompose at $T > 305$ °C releasing HAA (which is observed to be stable till $T = 480$ °C), radicals of acetylacetone, organic fragments of the ligand, and metal atoms.

So, the comparison of the results of the present investigation with the reported data suggests the following:

1) the compositions of the main gas-phase products and their fragmental ions in the case of thermal decomposition of the individual complex and in the case of its intercalate are similar to each other;

2) the decomposition of $Pd(AA)_2$ intercalated into the FG matrix occurs within a narrower temperature interval, at higher rate and is completed at lower temperature ($T = 200$ °C) than in the case of individual $Pd(AA)_2$;

3) the emission of ligand within the temperature range of 120–200 °C in the absence of the emission of any metal-containing fragments allows assuming that metal palladium remains in the FG lattice; as we have already mentioned, at this temperature the fluorographite basis of intercalates conserves its layered structure, and C/F ratio remains almost unchanged.

In our opinion, it is interesting to estimate and compare the ratio of concentrations $\alpha = [Pd(AA)_2]/[HAA]$ evolved in the gas phase during heating of the individual $Pd(AA)_2$ in the solid state and its intercalate. An estimation was performed using the integral intensity of ion current (I) corresponding to the evolved products. It should be noted that the intensity of ion current is proportional to the concentration of molecules $C = kI$, where k is the proportionality coefficient. One can see in Fig. 5 that in the case of individual $Pd(AA)_2$ (curve *1*) the relative content of acetylacetone is sub-
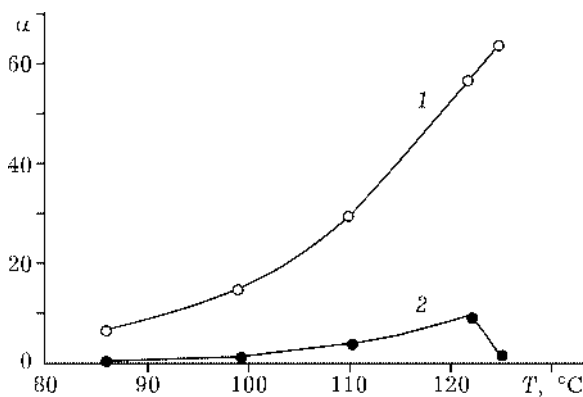

Fig. 5. Temperature dependence of the ratio of the evolved palladium complexes and acetylacetone in the gas phase (α) for individual (*1*) and intercalated $Pd(AA)_2$ (*2*).
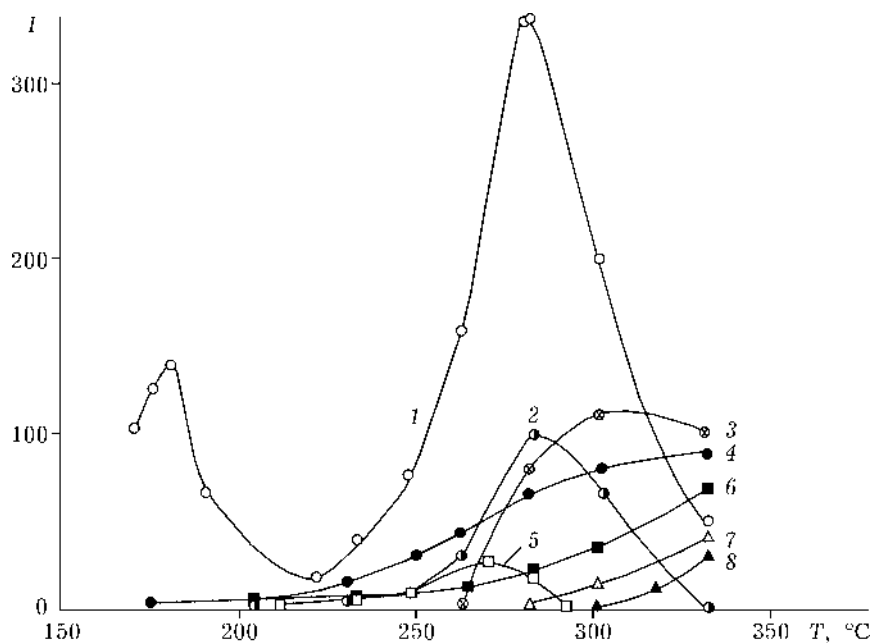
Fig. 6. Temperature dependence of the composition of the gas phase of intercalate with $CHCl_3$:
1 – $CHCl_3$, 2 – CF_2Cl, 3 – CCl_3, 4 – HF, 5 – $CHCl_2$, 6 – $CFCl_2$, 7 – C_2Cl_4, 8 – HCl.

stantially smaller than that in the case of intercalate (curve 2). For example, at $T = 87\,°C$, α for individual $Pd(AA)_2$ is 6.66, while for the intercalated compound it is 0.5. At the stepwise temperature raise, α for the individual compound is 3.57 within the temperature range of $86-134\,°C$, while for the intercalated compound it is 0.83 within the temperature range of $87-134\,°C$. Investigation of changes in the composition of the gas phase during thermal decomposition of the intercalate at fixed temperature allowed us to determine the optimal temperature range $(125-150\,°C)$ within which α reaches the smallest value about 0.2.

A question arises concerning the reason of a decrease in the stability threshold of the complex in the matrix. First of all, the effect of the second guest has to be excluded, because $CHCl_3$ molecules can be suppliers of hydrogen, at least at the first stage of thermolysis, which can lead to accelerated decomposition of the complex in the intercalated state. Starting from this assumption, we investigated thermal decomposition of $CHCl_3$ in the FG matrix. The composition of the gas phase, determined by means of mass spectrometry, is shown in Fig. 6. At the initial stage of thermolysis, the main products are $CHCl_2$, $CHCl_3$ and HF. At $T \geq 200\,°C$, $CFCl_2$ and CF_2Cl are ob-

served to appear in mass spectra; at $T > 250\,°C$, radical products (CCl_3) and C_2Cl_4 molecules appear; at $T > 300\,°C$, HCl is observed in mass spectra. At $T > 330\,°C$, mainly fluorocarbon derivatives of different composition are observed in the gas phase.

The analysis of the obtained results shows that thermolysis of intercalation compounds of FG with $CHCl_3$ is characteristic of hydrogen-containing guests [16] which under thermal action interact with the fragments of C–F matrix forming hydrogen fluoride at relatively low temperature $(\sim 100\,°C)$, as well as the products of interaction between the guest and the matrix (in the case under consideration, $CFCl_2$, CF_2Cl and CCl_3).

It should be noted that the data of mass spectrometric investigation of the gas phase during thermolysis of the intercalate with $CHCl_3$ were useful in the identification of such products as chloro-, fluoro-, and chlorofluoroderivatives of carbon in the case of thermolysis of the intercalate with $Pd(AA)_2$. Usually, $CFCl_2$ ions were absent from the mass spectra or their ion current was very small during the investigation of FG intercalates, similarly to CF_2Cl ions; the ions with $m/z = 66$ (CF_2Cl) and $m/z = 47$ (CCl) (see Table 1) had different composition, namely, COF_2 and COF [13, 15]. So, the comparison

between the data on gas-phase products of ther-molysis, obtained in the present work (see Fig. 2), and the literature data suggests that the origin of such ions as CF_2Cl, $CFCl_2$, $CFCl$, CCl_3, and CCl should be related to the interaction be-tween $CHCl_3$ and the matrix.

The following fact attracts our attention. The comparison between hydrogen fluoride libera-tion during thermolysis of intercalate with $CHCl_3$ (see Fig. 6) and intercalate with $Pd(AA)_2$, where $CHCl_3$ acts as a solvent (see Figs. 2, 4), reveals that in the latter case the amount of HF is much larger. This is evident, if we com-pare the curves of HF liberation shown in Fig. 4, or temperature dependence of $[CHCl_2]/[HF]$ ratio using the data shown in Figs. 6 and 2. Thus, chloroform does not have a decisive ef-fect on the liberation of HF in the case when $Pd(AA)_2$ is present in the FG matrix as solution in chloroform; the liberation of HF at $T > 120\,°C$ (see Fig. 2) is connected with the inter-action between C−F bonds of the matrix with C−H fragments of the ligand, which in turn leads to the decomposition of the complex. In our opinion, this explains the decrease in the stability of both the ligand and the complex itself in the FG matrix.

CONCLUSIONS

Thus, for intercalated $Pd(AA)_2$ as an exam-ple, a noticeable decrease in its thermal stability toward thermolysis in a two-dimensional mi-croreactor, FG matrix, is demonstrated. This feature can be useful for the use of FG inter-calates as precursors for the purpose of ob-taining new nanocomposite materials. It is evi-dent that the change in thermolysis conditions (temperature, atmosphere in which decompo-sition is performed, solvent with the help of which the substance is intercalated, the use of metal-containing compounds which are able to intercalate into the FG matrix without any solvent) will enable one to broaden substan-tially the range of composite materials obtained in a two-dimensional microreactor, *i.e.* fluori-nated graphite.

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