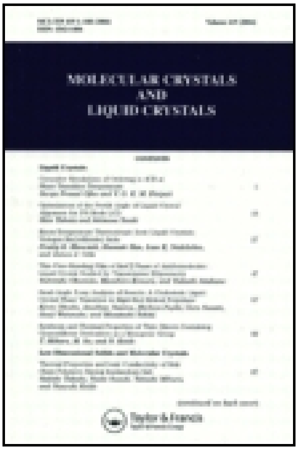

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Direct Oxidative Conversion of Graphite into Exfoliated Graphites. The Kinetic Model, Products, Mechanism

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DIRECT OXIDATIVE CONVERSION OF GRAPHITE INTO EXFOLIATED GRAPHITES. THE KINETIC MODEL, PRODUCTS, MECHANISM.

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Abstract. The process of thermally initiated synthesis of acceptor type graphite intercalation compounds (GICs) and the products of their thermolysis, *i.e.* exfoliated graphite (EG) has been considered within the scope of common kinetic model. Analysis of the data available in literature and results of present work indicate that in some cases direct oxidative conversion (DOC) of graphite into EG without specified GIC formation can be realized. DOC-process has been discovered for powder "graphite - $M^{2+}(NO_3)_2^-$" mixtures at the temperature $\geqslant 300^oC$. The conditions for DOC-process realization are considered.

INTRODUCTION

Exfoliated graphite (EG) is usually produced *via* heating intercalation compounds (GICs) up to temperatures between 150°C and 1300°C depending on the nature of intercalant.[1] This classic variant of the indirect graphite to EG conversion is combining sequentially two prosesses which are usually studied and considered as independent ones, i.e.

I – synthesis and isolation of GIC as an individual product;

II – GIC heating, EG obtaining.

However, there are some observations that may be identified as indications of direct graphite conversion (DOC).

DOC is direct EG formation in graphite reactions with oxidants without specified GIC obtaining and isolation. DOC process can be realized in mixtures of the type "graphite (G) – oxidative reagent (R)" for one of the following three cases:

a) oxidative gases, *e.g.* SO_3, N_2O_4, N_2O_5,[3]

b) graphite impregnated with Brønsted acids having oxidative properties, *i.e.* HNO_3, $HClO_4$, H_2SO_4,[4,5]

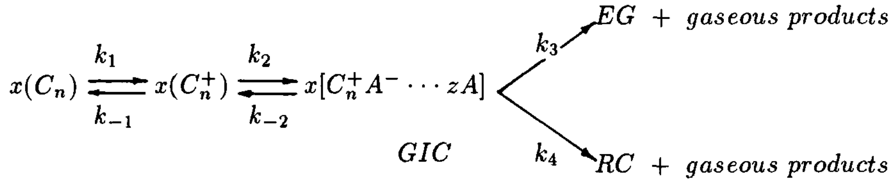
c) powder mixtures of graphite and Lewis acid, *e.g.* $FeCl_3$.[5]

The behaviour of such mixtures within a certain range of temperature is similar: graphite gets exfoliated very rapidly to yield EG as a single solid carbon product. It is only the nature of the reactant R that defines numerical values of the temperature range and the exfoliation degree estimated by K_V (*i.e.* exfoliation coefficient).

However, the above mentioned facts are not systematized and the phenomenon descriptions lack quantitative information. Nevertheless, such reactions are of great significance which explains our interest.

KINETIC MODEL

It is useful to consider the process of acceptor type GIC generation and exfoliation to EG within the scope of common kinetic model:



where $x(C_n)$ is graphite crystallite that includes x polyarene C_n layers with the number of C atoms being n per layer, A^- is an anion of Lewis or Brønsted acid, A, and RC are residue compounds.

The kinetic model includes the following steps:

1 – graphite oxidation with C_n^+ macrocations and $C_n^{+\cdot}$ radical cations formation as for individual arenes oxidation;[2]
2 – intercalation of A^- anions and A ligand-molecules into interlayer space;
3 – GIC exfoliation resulting in EG formation;
4 – thermal deintercalation without exfoliation resulting in RC formation.

The following two aspects are important for the realization of DOC: (i) proceeding of the process in kinetic area and (ii) experimental separation of the routes (3) and (4).

KINETICS OF NG THERMOLYSIS

The study has been carried out using a graphite nitrate[6] (NG) sample which is stable at room temperature but decomposes to EG and RC at 100 – 200°C. In isothermal conditions the yield of gases, m_g, increases monotonously to approach some m_g^∞ value which is the maximum for the given temperature T. With T increasing m_g^∞ increases too which is an evidence for participation of more and more structural centres in the reaction. However, the maximal yield of gas products (21 %, determined by heating NG up to 400°C) is not reached.

K_V parameter (determined by heating a sample at 500°C during 30 s) which characterizes exfoliation ability of GIC and depends on the intercalate content is also sensitive to thermolysis conditions. The plots of K_V *vs.* τ are of exponential form, K_V values are reduced with time but the state of initial graphite is not reached. Ultimate values of K_V (when $\tau \to \infty$) are different for various temperatures being located within the range of $K_V^\infty = 4 - 10$ cm^3/g.

Due to differences in K_V^∞ values it is expedient to establish an adjusted transformation degree $\alpha = (K_V^0 - K_V)/(K_V^0 - K_V^\infty)$, where K_V^0 is the initial value of the exfoliation coefficient at $\tau = 0$ ($K_V^0 = 70$ cm^3/g). The curves of α *vs.* τ are linearized in $ln(1-\alpha)$ *vs.* τ which allows to estimate effective rate constants of thermolysis, (h^{-1}): 0.31 ± 0.01 (130°C), 1.49 ± 0.04 (140°C), 2.15 ± 0.09 (150°C).

A time period, τ_α, required for achieving a definite transformation degree can be used as an autonomous kinetic characteristic (we assumed $\alpha = 0.35$, 0.50, and 0.65). The functions of τ_α *vs.* T in Arrhenius coordinates are linear. Besides, for the samples with different intercalate contents a compensative effect has been found which can be described as follows[6]:

$$lgA = (0.69 \pm 0.02) \; + \; (1.22 \pm 0.02) \cdot 10^{-4} \; E_{ef}$$

The effect is due to different numbers of thermolabile centres and to the entropy factor as it is typical for graphite reactions with CO_2 and H_2O at 400 - 1000°C.[7] The second reason is more sound since additional energy of any $C_n^+A^-$ centre formed with thermal excitation is averaged for the whole graphite lattice.

The data obtained confirm the fact that NG thermolysis at $T \leqslant 150^oC$ is controlled by chemical reactions in solid phase, *i.e.* by host lattice-intercalate bonds destruction. This statement is also supported by the following:

a) the process is independent of device characteristics [K_V *vs.* τ curves coincide in the adjusted coordinates α *vs.* $(\tau/\tau_{0.5})$][8];
b) linearization of temperature dependences for α and τ_α;
c) compensative effect and similarity of E_{ef} values determined by various methods (kJ/mol): 130 ± 20 (derivatography), 140 ± 20 (by α), 130 ± 10 (by τ_α);
d) coincidence of E_{ef} with the energies typical for thermolysis of individual compounds, e.g. HNO_3 (≈140 kJ/mol), $Mg(NO_3)_2$ (116 kJ/mol), $Fe(NO_3)_3$ (124 kJ/mol).[9]

Besides, calculations using a topokinetic equation $\alpha = 1 - exp(-k\tau^n)$ with $\alpha <$ 0.65 yielded $n \geqslant 1$ (especially for $\alpha \leqslant 0.35$) which is also a good reason to believe that the thermolysis area of NG is a kinetic one.[6]

SEPARATION OF EG AND RC FORMATION ROUTES

Both routes of thermolysis, *i.e.* deintercalation to RC and EG formation, are followed by gaseous products evolution. Therefore it is difficult to separate them using this parameter. Their contributions have been estimated using the following approach: GIC volume does not change with deintercalation against a background of gaseous products formation, whereas EG formation is accompanied by a volume increase with the same kinetics of gas evolution. Comparison of data for K_V *vs.* τ and m_g *vs.* τ at $T = const$ allowed to separate routes (3) and (4). Linear plots of K_V *vs.* m_g (Fig. 1a,b) show proceeding of at least two different processes.

In the first region no changes are practically observed, though gas evolution proceeds at maximal rates, and thermolysis is controlled by deintercalation. In the second region, at lower rates, gas evolution initiates exfoliation, with the inclination growing symbatically to temperature.

For the process of EG formation the first region is the induction period (τ_i). With the increase of thermolysis temperature from 100°C up to 150°C τ_i value decreases from 60 h. to 5 min. Dependence in $ln\tau_i$ *vs.* T^{-1} coordinates is linear (Fig. 1c). E_{ef} = 140 ± 25 kJ/mol coincides with the data obtained by other methods. The curves shown in Fig. 1 could be interpreted as sequential processes of deintercalation (step 3) and exfoliation (step 4). However in this case it would be difficult to account for the absence of exfoliation during the initial period, when the rate of gas emission is maximal. It is more likely that steps (3) and (4) are parallel, but with different temperature dependences of k_3 and k_4. An increase in temperature leads to domination of route (3), and the induction period of EG formation decreases. Additional temperature rise up to 500°C (conditions for K_V determination) provides maximal favourable conditions for step (3), and EG yield is nearly quantitative.

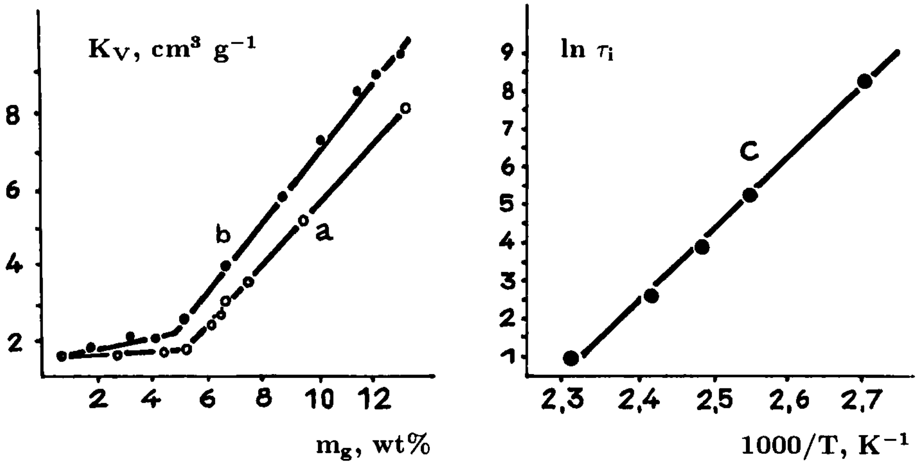


FIGURE 1. Plots of exfoliation coefficient, K_V, *versus* yield of gases, m_g, at 130°C (*a*) and 140°C (*b*) and $ln\tau_i$ *versus* T^{-1} (*c*).

PRODUCTS YIELD RELATIONSHIP

Compositions of solid thermolysis products in "G - R" mixtures are determined by using the relationship between the rates $W_1 - W_4$ (see the scheme) which depend on temperature (T) and heating rate. The evidence[2-5,11] for the influence of these factors on the concentrations [GIC], [EG], and [RC] in the heating system permits to present qualitatively the form of the function [P] = $f(T)$ where P = GIC, EG, RC at $\tau = const$ (Fig. 2).

Variant A in Fig. 2 exhibits "classical" stepwise transition of graphite into EG. The temperature regions corresponding to GIC and EG synthesis do not overlap. Interaction of graphite with an oxidant over the temperature range ΔT_{GIC} results in GIC formation with the reaction arrested. The current [GIC] concentration is defined by the ratio W_2/W_{-2}. If a compound obtained in ΔT_{GIC} is placed into a temperature region ΔT_{EG}, one observes a thermal expansion effect and EG and RC are formed with the concentrations defined by W_3, W_4, and W_2 ratios.

There is an intermediate area $\Delta T_{mid.}$ where GIC and EG are not formed due to the fact that the equilibrium of steps (1) and (2) is shifted to the left whereas the temperature range of EG formation has not been reached. This variant has been studied for various "G – R" systems where R = HNO_3, H_2SO_4 – Cr(VI), H_2O_2 – H_2SO_4, SO_3, N_2O_5, $FeCl_3$, *etc.*[2–5] and implemented to produce EG on industrial scale.[10]

There is one more kinetically feasible variant of the scheme, when the temperature conditions of GIC synthesis and its thermal expansion coincide, i.e. $\Delta T_{GIC} = \Delta T_{EG}$ (Fig. 2, variant B). In this case, only thermally stable products, *i.e.* EG, can be observed, whereas intercalation compounds exist in the form of a highly unstable intermediate. Therefore we deal with direct one-step transition of graphite into EG. This behaviour was described elsewhere, e.g. for graphite mixtures with H_2SO_4,[4,5] Cl_2O_7,[11] or ternary systems "G – HA – H_2O" with HA = HNO_3, $HClO_4$.[4,5]

T_{GIC}^{max} is the temperature of achieving the maximal GIC yield at a maximal rate;

T_{EG}^{max} is the temperature of effective exfoliation with only EG observed in the system, *i.e.* the condition $k_3 \gg k_4$ and k_{-2} is met.

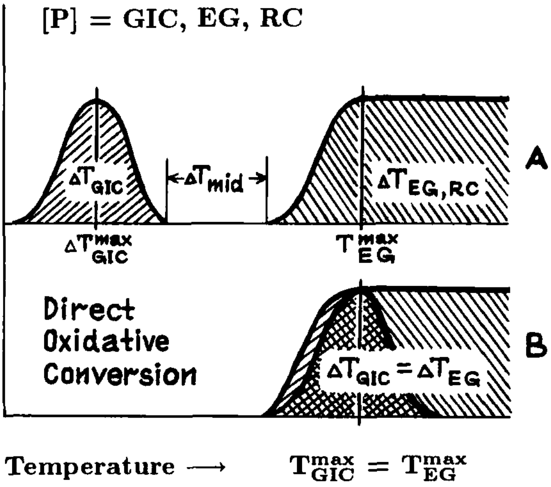


FIGURE 2. Theoretical temperature dependences of graphite intercalation compounds (GICs) and exfoliated graphite (EG) yields. Comparison of indirect, i.e. stepwise (A) and direct, i.e. one-step (B) oxidative conversion.

CONDITIONS FOR DOC REALIZATION

The DOC process is possible under the following conditions of rate (W_i) ratios for individual steps:

a) the rate of step (3) is equal or higher than that for GIC formation, *i.e.* $W_3 \geqslant W_2$ when $W_3 > W_4$;

b) GIC intermediate formation and EG generation occur at high rates;

c) rates of opposite reactions, W_{-1} (carbocation reduction) and W_{-2} (deintercalation), are negligible.

A priori selection of reagents is based on several principles. First, in temperature conditions of DOC process an oxidative reagent is necessary to provide an intensive removal of electrons from graphite. Beyond the area of ΔT_{EG} the reagent should have low oxidative ability, and it is only in EG formation region that it should have a relatively high oxidative ability. Second, for realization of step (2) high concentrations of A^- anions and other intercalates are necessary, with the temperature areas of electron transfer, anions generation and thermal decomposition of GIC coinciding.

For example, for "G – H_2SO_4" system no reaction is observed up to 200°C due to low oxidative ability of H_2SO_4. If graphite is additionally oxidized electrochemically,[2] graphite bisulphate is formed rapidly and almost quantitively. However, if the "G – H_2SO_4" system is placed into ΔT_{EG} area, DOC process proceeds with EG formation.[4,5]

Seeking for reagents satisfying the developed criteria, a number of "G – MA_2" systems, where M^{2+} is an alcaline earth metal and A^- is an anion of an oxygen–containing Brønsted acid (NO_3^-, ClO_3^-, *etc.*), have been found for which only DOC process can be realized. For example, when heating (300 – 700°C) graphite and zinc or magnesium nitrates, graphite quickly (within seconds) transforms into EG; the maximal values of K_V^{max} are 80 and 40 cm^3/g, respectively. Experimental dependences of K_V/K_V^{max} on temperature and salt concentration in mixtures (Fig.3) are similar to those in the theoretic variant B (Fig. 2). According to X–ray diffraction analysis, GIC is not formed.

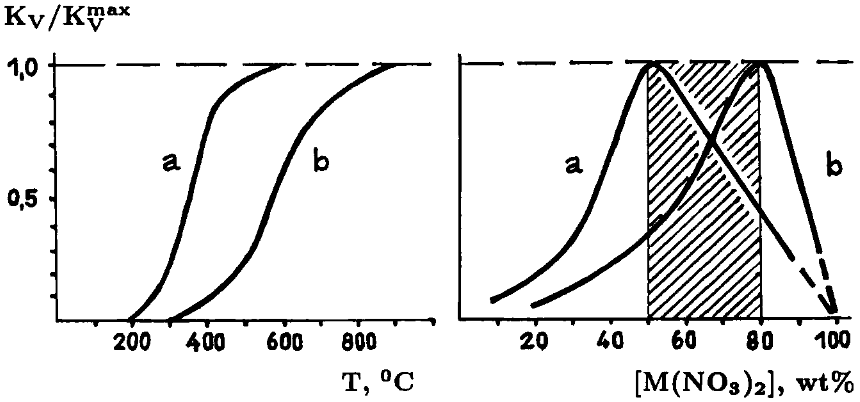


FIGURE 3. Effects of temperature and salt content on the K_V/K_V^{max} ratio for "graphite – $Zn(NO_3)_2$" (*a*) and "graphite – $Mg(NO_3)_2$" (*b*) mixtures.

The model of the reaction mechanism in solid state for the "G – $M(NO_3)_2$" system is based on the data of salt thermolysis. $M(NO_3)_2$ thermolysis starts from salt melting in crystallization water, and a partial dehydration of salt occurs along with an increase in temperature, then dehydration process accompanied by the evolution of nitric acid into gas phase proceeds in parallel to salt decomposition. Meanwhile oxy– or hydroxynitrates and O–atoms may form as intermediates. The final solid product is MO. O_2, N_2, NO_2, N_2O_3, N_2O_4, N_2O_5, H_2O are registered among final gaseous products.

Nitric acid formed during "G – $M(NO_3)_2$" system thermolysis as an intermediate product reacts with graphite in a liquid melt and/or gaseous phase according to the well-known Forsman scheme[12]:

$$
\begin{aligned}
&2HNO_3 \rightleftarrows NO_3^- + NO_2^+ + H_2O \\
&C + NO_2^+ \longrightarrow C_n^+ + NO_2 \\
&C_n^+ + NO_3^- + mHNO_3 \longrightarrow C_n^+NO_3^- \cdot mHNO_3
\end{aligned}
$$

O–atoms or N_2O_5 as an intermediate product of thermal decomposition of nitric acid may act as a graphite matrix oxidant.

Thus, within "G – $M(NO_3)_2$" system oxidants and anions indispensable for DOC process are formed. The following evidence is in favour of the above mentioned mechanism:

a) graphite thermodestruction acceleration (derivatography);
b) generation of NO_2 and MO formation;
c) graphite exfoliation as an indirect proof of GIC formation, *e.g.* $C_n^+NO_3^-$;
d) burning out of a portion of graphite to CO and CO_2, which is in linear dependence on MA_2 content and indirectly indicates appearance of O–radicals;
e) essential influence of the cation nature (Fig. 3) determining starting salt thermolysis.

We believe that detailed investigations of the above discussed and similar systems might be useful for developing new technologies of EG production.

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