Intercalation Compounds of Trimethylphosphate in Graphitic Oxide

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Abstract. The intercalation compounds of trimethylphosphate (TMP) in graphite oxide (GO) have been synthezized. Two compounds have been characterized, corresponding to intercalation of one or two molecules of TMP, and have been characterized by gravimetric adsorption, X-ray diffraction and infrared spectroscopy. Bonding between TMP and graphitic oxide takes place through hydrogen bonding with OH groups of the layered material.

1. Introduction

Graphitic oxide (GO) is a widely studied material because of its importance, both from a theoretical point of view, because of its structure and textural properties, and its applications in different industrial processes [1–7], which are mainly due to its layered structure and ability to adsorb polar substances by interaction with hydroxyl groups of the interlayer space. This is a behaviour which is fairly similar to that observed with layered silicates.

The interactions between GO and amines [8], alcohols [9, 10], and other polar molecules [11, 12] have been studied by several authors, and we have previously synthesized and studied the intercalation compounds formed by GO with several sulfoxides [13–16], the amount of polar liquid retained, and the most probable orientation of such molecules in the interlayer spaces of GO being determined using different techniques.

In the present paper, the synthesis and characterization of intercalation compounds between GO and TMP, as well as the effect of several treatments on the formation of such compounds, are studied.

2. Experimental

2.1. MATERIALS

The graphite was from Rindorffwerke, with an average particle size of 760 μm. The preparation of the oxide has been described elsewhere [17]. TMP was from Fluka, purity pract. and density 1.21 g cm^{-3}.

2.2. APPARATUS

The amount of TMP retained in the interlayer space was determined following Jolly's balance method [18] in a thermostatted adsorption chamber provided with a calibrated quartz spiral

from Thermal Syndicate Ltd. (sensitivity of 39.2 cm g^{-1}) connected to a conventional Pyrex high vacuum system.

X-ray diffraction diagrams were recorded in a Siemens mod. Kristalloflex 810 instrument, using a powder camera, 114.8 mm diameter, and Ni filtered CuKα (λ = 154.050 pm) radiation, while the IR spectra were recorded in a Beckman mod. Acculab 10 spectrophotometer.

3. Results and Discussion

3.1. GRAPHITIC OXIDE

A basal spacing of 749 pm was obtained for GO (taking into account that the width of the carbonaceous layer is 480 pm [19–21]) indicating, that the GO corresponds to a water molecule monolayer interlamellar compound [14, 15, 21].

3.2. FORMATION OF INTERLAYER COMPOUNDS

Prior to adsorption, the GO sample was outgassed at 295 K and 10^{-2} Pa to a constant weight. The interlayer compounds were prepared following two different methods:

(A) Room temperature impregnation followed by isothermal desorption at 295 K and 10^{-2} Pa.

(B) Adsorption from the gas phase.

Following method A, the effect of the impregnation time prior to desorption on the nature of the final intercalation compounds was studied. So, samples of GO were immersed in TMP for $3/4$, 2, 4, and 8 days, and then were outgassed at 295 K and 10^{-2} Pa. A weight loss was observed in all four cases until a constant weight (corresponding to adsorption of 757–779 mg TMP/g GO, see Table I) was reached after 60–70 h desorption, Figure 1. The
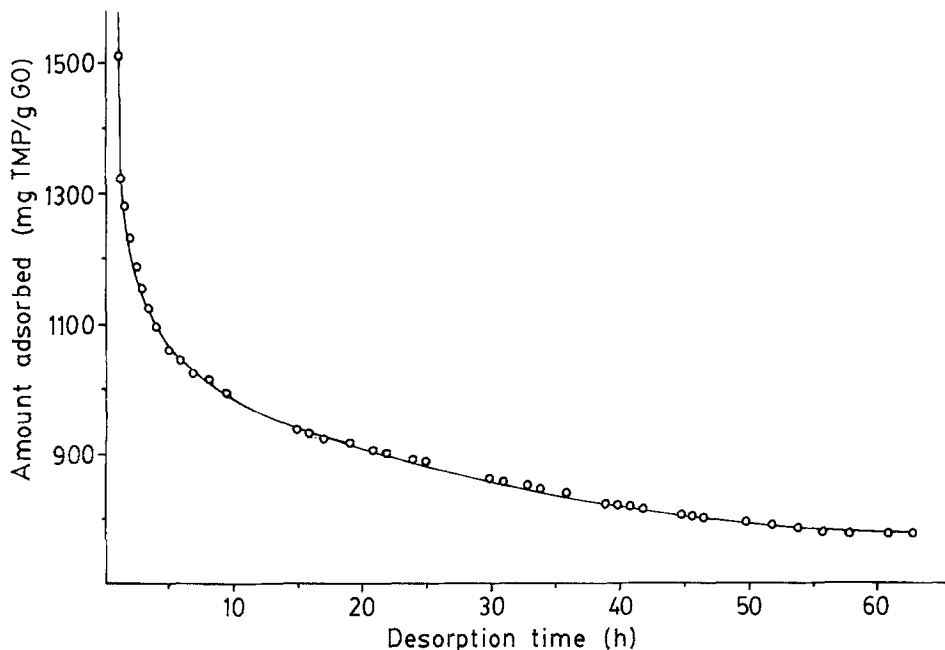

Fig. 1.   Desorption isotherm (295 K) of TMP from GO immersed for 2 days in TMP (Sample A-2).

Table I. Interlayer spacings, amounts of TMP retained, and accesible surface area of TMP/GO intercalation compounds.

Samples	2θ	d(pm)	Interlayer space available for TMP (pm)	$\dfrac{\text{mg TMP}}{\text{g GO}}$	$S_{int}(\text{m}^2\text{g}^{-1})$
A3/4	7.30	1209	729	757	1601
A2	7.45	1186	706	774	1637
A4	7.30	1209	729	776	1620
A8	7.35	1205	725	779	1648
B(1 Pa)	5.55	1590	1110	1548	1637
B(1–2 × 10^3 Pa)	5.47	1620	1130	1552	1642

interlayer spacings in these samples, ranging from 1186 to 1209 pm, has also been included in Table I.

The amounts of TMP retained after several immersions and desorptions at 10^{-2} Pa are close to 768 ± 11 mg TMP/g GO, thus suggesting that 18 h immersion followed by desorption is enough to obtain sample A.

In order to check the effect of the initial pressure on the nature of the intercalation compound, experiments following method B were carried out at a total initial pressure of $1–2 \times 10^3$ and 1.3 Pa. After a constant weight was reached, the TMP container was removed and the system outgassed at $1–2 \times 10^3$ Pa (or 1.3 Pa) in order to eliminate the excess of adsorbate (leading to a slight weight loss, see Figure 2), until a limiting weight of 1550 ± 2 mg TMP/g GO was reached (Table I), this value being about twice the amount retained by the sample obtained following method A.
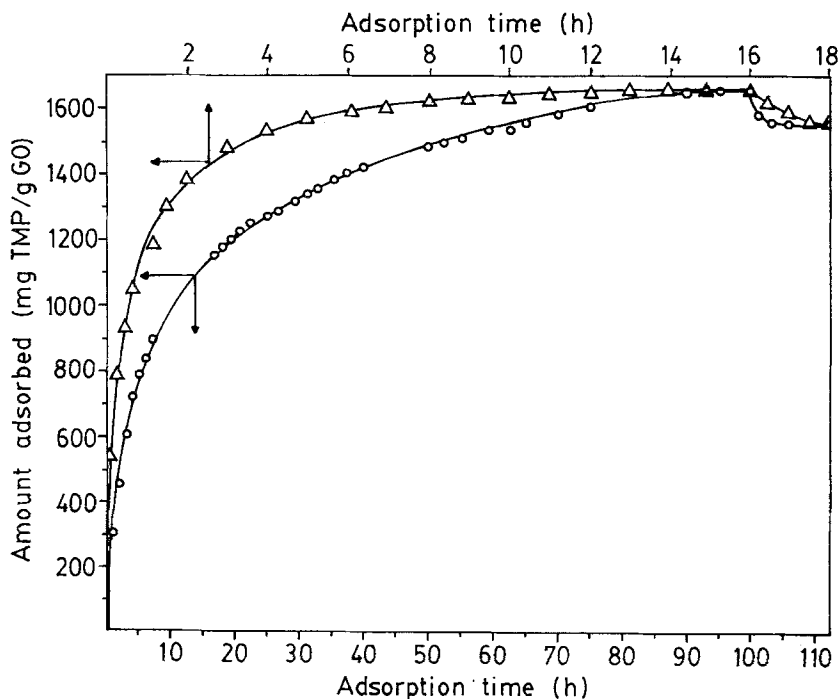

Fig. 2. Adsorption isotherms (295 K) from the gas phase on GO; △ Sample B (1 Pa); O Sample B (1–2 × 10^3 Pa).

Interlayer spacing for samples obtained following method B were 1590 and 1620 pm (also included in Table I). Similarly to data obtained with samples A, the initial pressure (in the range here studied) has no effect on the nature of the intercalation compound obtained, although the time needed to reach the equilibrium is different in both cases.

The increase in the interlayer spacing along direction c of GO indicates it is swelling as a result of the TMP adsorption, probably removing the water molecules [14, 15] because of the large dipole moment of TMP (3.02 D) [22, 23]; taking into account the width of the carbonaceous layer (480 pm), the interlayer space for adsorbed molecules is 720 pm for samples A and 1110 pm for samples B (Table I), corresponding to the formation of monolayer and bilayer compounds, respectively (Figure 3). Although structural data for TMP are scarce
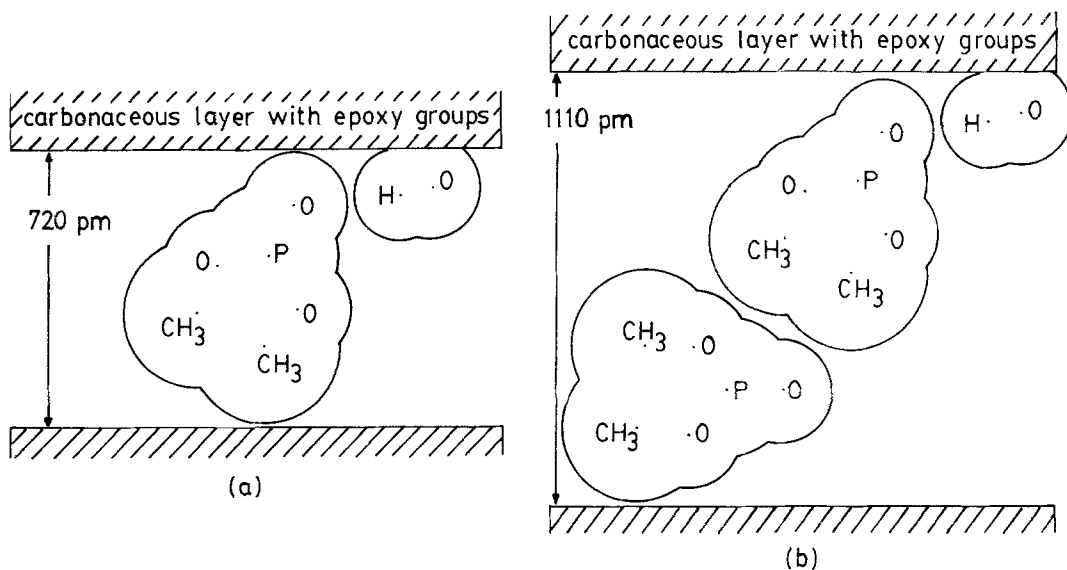

Fig. 3.   Most probable orientation of TMP molecules in the interlayer space of GO; (a) Monolayer compound, Sample A; (b) bilayer compound, Sample B.

in the literature, if those for triphenylphosphate [24, 25] and the spatial configuration given by Aroney *et al.* [26] are considered, the molecular geometry of TMP can be determined using scale models, resulting in a planar projection of 24.6×10^4 pm^2 and a height of 707 pm.

In order to check the reversibility of the formation of the monolayer and bilayer compounds, a desorption-adsorption-desorption cycle (Figure 4) was carried out on samples of GO immersed in TMP for 48 h.

Once a monolayer compound has been synthesized following method A (first desorption step at 10^{-2} Pa), an increase in the weight of TMP retained by GO is observed during the adsorption step ($1-2 \times 10^3$ Pa), reaching a limiting value of 1552 mg TMP/g GO, while during the second desorption step at 10^{-2} Pa (third step of the whole process) a fast weight loss is observed, until a constant weight corresponding to 774 mg TMP/g GO is reached. These amounts match very well with those previously obtained for the monolayer and bilayer compounds (1550 and 768 mg TMP/g GO), and their ratio equals 2; moreover, the interlayer spacings for these samples were 735 and 1620 pm, which is in very good agreement with those of samples obtained by methods A and B, respectively.
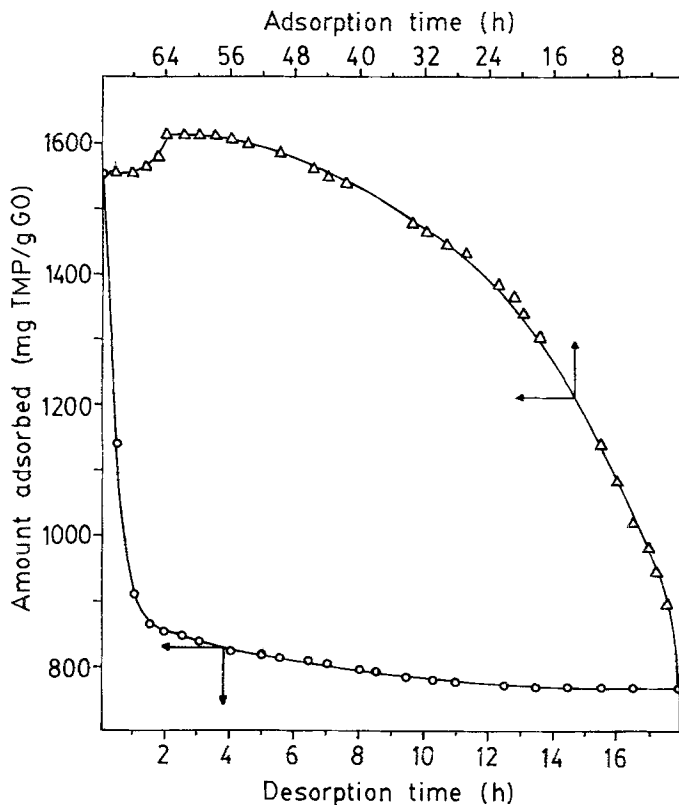
Fig. 4.   Desorption-adsorption-desorption cycle (295 K) of TMP on GO;
△ adsorption (1–2 × 10³ Pa); ○ desorption at 10⁻² Pa (third step).

Taking into account the amounts of TMP adsorbed in the interlayer spacings of samples A and B, and the surface covered by a molecule of TMP (24.6 × 10⁴ pm²), the accessible surface area of GO to TMP has been calculated using the Lopez–Gonzalez *et al.* equation [27] to be 1625 ± 24 m²/g GO (Table I) which is in good agreement with those values reported in the literature for well-oxidized graphitic oxide [28, 29] and those supporting the orientation of the TMP molecule depicted in Figure 3.

In order to check the way the TMP molecule binds to GO, the IR spectra of samples A and B (monolayer and bilayer, respectively) as well as that of pure TMP have been recorded (Figure 5); bands in the 1300–1200 cm⁻¹ range correspond to the P = O stretching mode. Such a band is recorded at 1280 cm⁻¹ in TMP [30] and shifts to lower wavenumbers while increasing its intensity when adsorbed on GO. This shift indicates a decrease in the electron density of the P = O bond, thus suggesting that the interaction with the layered material takes place through the lone pairs of the oxygen atom in the TMP molecule; on the other hand, the increased intensity of this band has been attributed [31] to the formation of hydrogen bonds with the hydroxyl groups of GO as a result of resonance phenomena similar to the keto-enolic tautomerism.

The shift and the increase in intensity are more pronounced for samples A, while the bands are ill-defined at 1260 cm⁻¹ for samples B and its intensity is only about 77% of that of samples A. These results can be easily interpreted by assuming that only one of the two
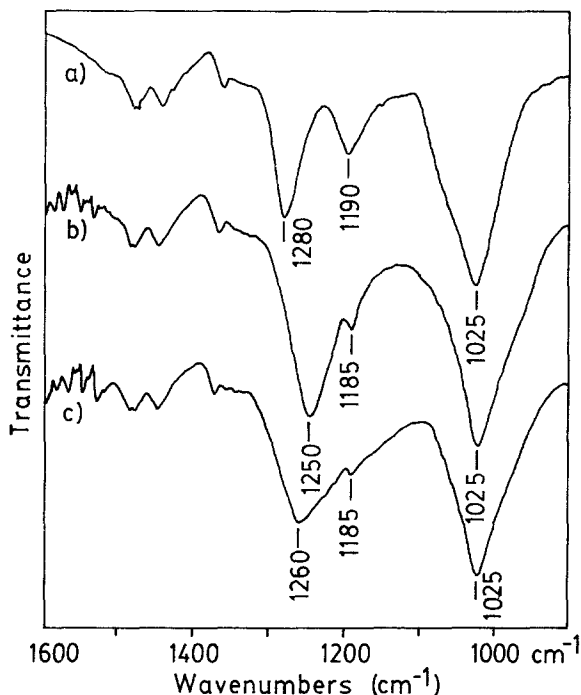
Fig. 5.   Infrared spectra of TMP/GO intercalation compounds;
(a) TMP; (b) monolayer compound, Sample A;   (c) bilayer
compound, Sample B.

molecules of TMP existing in samples B, strongly interacts with GO as in samples A, while
the other is simply interacting through weak van der Waals forces, both with the GO layer
and with the other TMP molecule thus weakening the GO–TMP hydrogen bonding and
leading to a frequency distribution in the range 1280–1250 cm^{-1} (Table II).

Table II.   Infrared data for TMP/GO intercalation compounds

Sample	$\delta_{CH_3}^a$ asym	$\delta_{CH_3}^a$ sym	$v_{P=O}^a$	Relative intensity $v_{P=O}$	$\Delta v_{P=O}^a$	v_{P-OCH}^3 asym	v_{P-OCH}^3 sym
TMP	1440 (w)[b]	1360 (vw)	1280 (m)	100		1190 (m)	1025 (s)
monolayer TMP/GO	1440 (w)	1360 (vw)	1250 (s)	147	30	1185 (m)	1025 (s)
bilayer TMP/GO	1440 (w)	1360 (vw)	1260 (s)	130	20	1185 (m)	1025 (s)

^{a} cm^{-1}; ^{b} w = weak, vw = very weak, m = medium, s = strong.

On these grounds, it can be concluded that in the monolayer compound (sample A) the
molecules of TMP strongly interact with the hydroxyl groups of the GO layers, while in
samples B, in addition to such strongly interacting molecules, the other TMP molecules are
bonded only through weaker van der Waals forces and, thus, are easily removed.

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