CHEMISTRY OF GRAPHITE INTERCALATION BY NITRIC ACID

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Abstract—Gas-phase intercalation of graphite by nitric acid is accompanied by evolution of a brown gas which has been identified as nitrogen dioxide by chemiluminescence measurements. The reaction is inhibited by the presence of oxygen or water vapor, but not by nitrogen. These results, and the existence of induction times of 5–20 min before intercalation begins, is interpreted as evidence that intercalation is effected by oxidation of graphite by adsorbed nitronium ions with the release of NO_2. The graphite lattice then intercalates NO_3^- ions along with neutral HNO_3 molecules.

1. INTRODUCTION

The structure and properties of so-called graphite nitrate have been subjects of considerable interest over the last decade [1–8]. During this same period, however, little has been reported concerning the details of various chemical phenomena associated with the preparation of this intercalation compound. The purpose of this research was to observe the effect of diluent gases on the reaction of highly oriented pyrolytic graphite with HNO_3, and to identify a brown gaseous by-product of the intercalation reaction that we suspected was NO_2.

2. EXPERIMENTAL

Intercalation reactions were followed gravimetrically. The experimental set-up is shown in Fig. 1, and is similar to that used by Ubbelohde [1]. Highly oriented pyrolytic graphite (HOPG) samples were placed on the quartz pan of a quartz spring balance enclosed in a glass inter-calation chamber. The intercalation chamber was connected to a glass vacuum manifold by a vacuum stopcock. The pressure in the manifold was measured with a mercury manometer and (when checking the vacuum system for leaks) a McLeod gauge.

Oxygen and nitrogen could be admitted to the manifold through vacuum stopcocks. Water vapor could be admitted by opening the manifold to a flask containing liquid water in equilibrium with its vapor.

The HOPG, which was supplied by Union Carbide Corporation, was stored in a desiccator over $CaCl_2$ and was given no pretreatment. Chips of about $1.0\ cm^2$ area and $0.1\ cm$ thickness were used. For all the experiments except the one designed for NO_2 identification, the nitric acid was prepared by distilling reagent grade 96% HNO_3 as suggested by Fuzellier [9]. In this last experiment, HNO_3 was distilled from a mixture of reagent grade potassium nitrate and 98% sulfuric acid. Oxygen was
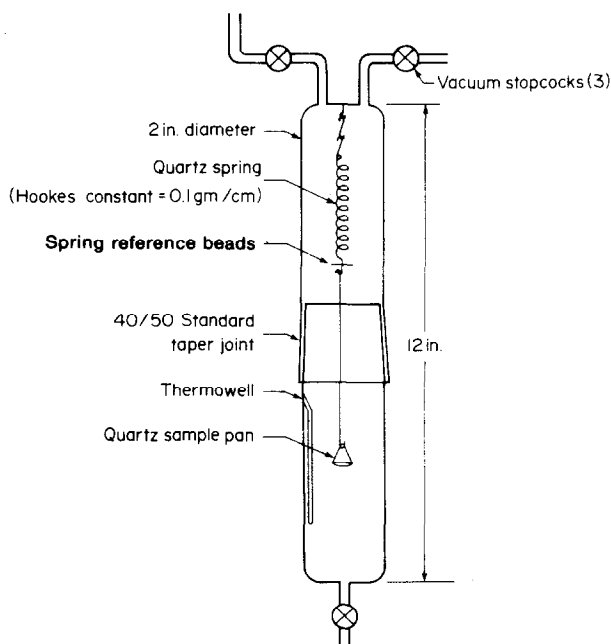

Fig. 1. Apparatus for intercalation measurements.

commercial AIRCO bottle gas and nitrogen was commercial "dry" grade. Distilled water was used in the experiment to determine the effect of H_2O vapor on intercalation by HNO_3.

Before an intercalation experiment was run, the HOPG sample was placed on the balance pan, the vacuum system (including manifold and intercalation chamber) was evacuated, "flamed" out with a 20 ampere heat gun, and checked for leaks. The initial height of the pan was then measured with a cathetometer. The manifold and intercalation chamber were opened to the acid reservoir, and the height of the pan followed with the cathetometer.

Typical curves of increase in weight as functions of time are shown in Fig. 2. Induction periods up to 20 min were observed.

To check the effect of diluent gas, after the intercalation chamber had been flooded with HNO_3 the pressure of the system was increased by bleeding in N_2 or O_2, or in the case of water vapor by opening the system to the water reservoir.

In every experiment, intercalation was accompanied by generation of a brown gas in the intercalation chamber. Blank runs, i.e. those for which no graphite sample was placed on the pan, gave no evidence of a brown gas, indicating that this by-product was generated by intercalation and not by decomposition of the nitric acid. To prove that the brown gas was indeed NO_2, the reaction products after one experiment were flushed through a REM NO_x analyzer[10] with a stream of helium. As operated, the NO_x analyzer was specific for NO_2. The experimental set-up is shown in Fig. 3.

The gas stream was first passed through a trap containing solid NaOH deposited on the inside surface

from aqueous solution, and then dried with an open flame. The trap effectively removed all of the HNO_3 from the gas stream allowing most of the NO_2 to pass. Calibration experiments with NO_2 from Matheson Gas Products indicated that some of the NO_2 was also lost in NaOH trap. This made it impossible to use the chemiluminescence technique as a quantitative analysis for NO_2; clearly, however, the NO_2 concentration in the intercalation chamber after the reaction was at least as great as the value calculated assuming no loss in the NaOH trap.

After leaving the NaOH trap, the argon carrier stream passed through a glass tube maintained at 180°C with a heating tape, where the following reaction went to 5–10% completion:

$$2NO_2 \rightarrow 2NO + O_2.$$
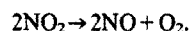
The stream was then mixed with ozone in the analyzer, which effected the reaction

$$NO + O_3 \rightarrow NO_2^* + O_2$$

where NO_2^* is nitrogen dioxide in an excited state. The NO_2^* drops to NO_2 in the ground state as the gas continues to pass through the instrument, and the chemiluminescence produced by this reaction is detected by a photomultiplyer tube in the instrument. The signal was displayed on the instrument and detected with a Sargent recorder. Calibration experiments indicated that the output of the instrument and recorder were proportional to the concentration of the NO_2 in the gas stream entering the instrument.

RESULTS AND DISCUSSION

Typical curves of increase in weight as functions of time in the absence of diluent gas are shown in Fig. 2. In each intercalation experiment, an induction time of from 5 to 20 min was observed before there was a detectable weight increase of the graphite specimen. And for each experiment, we observed the presence of a brown gas in the intercalation chamber within 5–10 min after the end of the induction period.

In the experiments using diluent gases, the acid was kept at 0°C (giving an HNO_3 vapor of about 13 Torr) and the graphite at 20°C. As shown in Fig. 2, these conditions are associated with intercalation going to completion at fourth stage. The intercalation system was first allowed to come to equilibrium at the vapor pressure of HNO_3. Then nitrogen or oxygen was introduced to bring the total pressure up to 1.0 atm, or else the system was opened to the water reservoir and the total pressure allowed to approach the sum of the vapor pressures of HNO_3 and H_2O.

After introducing nitrogen, the weight of the graphite specimen increased slowly as is shown in Fig. 4. We note that after an induction period of about 15 min, the intercalation reaction began. The rate decreased markedly after about 200 min, however, and became limited by the rate at which HNO_3 at about 13 mm Hg pressure could diffuse through 1.0 atm of nitrogen to reach the graphite sample.
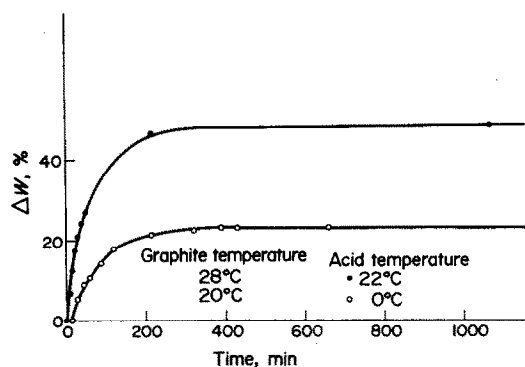

Fig. 2. Typical intercalation results; percent increase in weight of HOPG as functions of time.
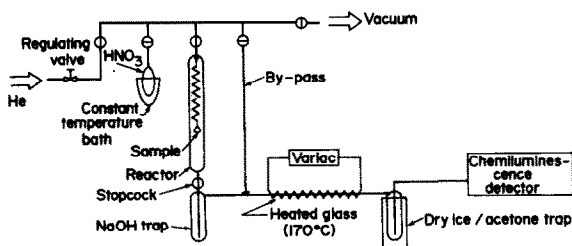

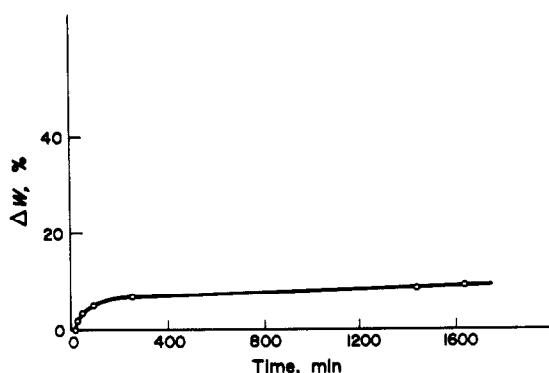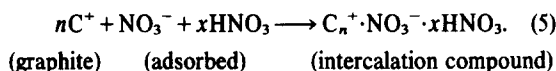Fig. 3. Intercalation apparatus with provision for NO_2 analysis by chemiluminescence measurement.
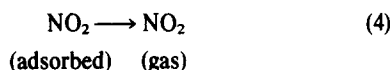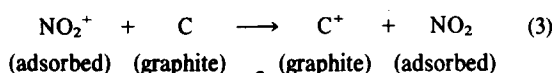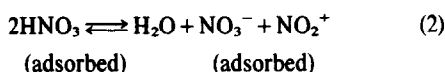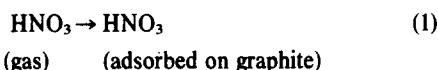
Fig. 4. Diffusion hindered intercalation by nitric acid in the presence of nitrogen. Total pressure = 1.0 atm.

When the experiment was repeated using O_2 instead of N_2 no intercalation was observed over a 24 hr period. Likewise, when H_2O vapor was introduced, no intercalation was observed for 24 hr. After completing the experiments using O_2 and H_2O as diluent gases, the system was re-evacuated and then filled with HNO_3 vapor. Intercalation reactions then ran normally, indicating that there was nothing peculiar about the HOPG samples used in these experiments. We conclude, therefore, that H_2O vapor and O_2 inhibit intercalation, but that N_2 does not.

For the identification of the by-product gas, a sample was intercalated until the weight gain was consistent with a stage 2 compound. Analysis of the reaction gas gave 0.134 mg of NO_2 per mg of intercalant.

We infer from these experiments that there is an essential chemical mechanism associated with intercalation of graphite by nitric acid. The most plausible is the following:

$$HNO_3 \rightarrow HNO_3 \qquad (1)$$

(gas)   (adsorbed on graphite)

$$2HNO_3 \rightleftharpoons H_2O + NO_3^- + NO_2^+ \qquad (2)$$

(adsorbed)   (adsorbed)

$$NO_2^+ + C \longrightarrow C^+ + NO_2 \qquad (3)$$

(adsorbed) (graphite)   (graphite) (adsorbed)

$$NO_2 \longrightarrow NO_2 \qquad (4)$$

(adsorbed)   (gas)

$$nC^+ + NO_3^- + xHNO_3 \longrightarrow C_n^+ \cdot NO_3^- \cdot xHNO_3. \qquad (5)$$

(graphite)   (adsorbed)   (intercalation compound)

Reaction 2 is an adsorbed-phase reaction analogous to the well-known dissociation of pure nitric acid, and generates the highly electrophylic nitronium ion, NO_2^+. Reaction 3 shows the nitronium ion capturing an electron from the graphite lattice, and then desorbing as NO_2 (Reaction 4). As the graphite becomes positive it draws in nitrate ions (along with neutral HNO_3 molecules) to maintain electrical neutrality. Inhibition of H_2O vapor is explained by assuming that water adsorbed at the vapor-

graphite interface forces Reaction 2 to the left.

Inhibition by oxygen and the observed induction times are consistent with Reaction 3 if we assume that NO_2^+ captures unpaired electrons from the graphite. If such unpaired electrons exist around the periphery of hexagonal arrays in the graphite lattice they could associate with adsorbed oxygen molecules (which demonstrate partial free radical character) and become unavailable for reaction with NO_2^+. Furthermore, the presence on the graphite surface of other inhibitors of free radical reaction could inhibit the intercalation reaction until they are destroyed by reaction with NO_2^+. There is a subtile phenomenon associated with the intercalation that should be reported. After the intercalation reaction is well underway, and the brown gas fills the reaction chamber, a fog deposits as a ring on the inside wall of the intercalation chamber at level of the graphite sample. This is undoubtedly water formed in Reaction 2, which, of course, then dissolves HNO_3 to form a film of concentrated nitric acid.

Ubbelohde[1] reports that x in Reaction 5 should be equal to 3. Direct determination of the NO_2 generated in the formation of a stage two compound gives results more consistent with x equal to 4.5. We know, however, that some NO_2 is lost as the gas passed through the NaOH trap. We would thus expect a value of x calculated by assuming that all NO_2 generated by the reaction passes through the detector would be too large. We thus conclude that, in the formation of a stage 2 compound, x in eqn (5) can be no larger than 4.5.

In conclusion, we should like to add that the observed oxidation of graphite by nitric acid is in agreement with a more general picture of intercalation to form so-called "acceptor compounds"[11]. Indeed, in this example, the use of the term "acceptor compound" is inappropriate since there is no electron transfer between graphite and intercalant. Instead, electrons from the graphite lattice are lost to an electrophylic species, NO_2^+.

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