# The Reaction of Active Nitrogen with Graphite

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The reaction of microwave-activated nitrogen with graphite was studied in the temperature range 1694 to 2365°K. Cyanogen, hydrogen cyanide, and carbon dioxide were the reaction products condensed in traps at liquid nitrogen temperature. Activation energies of  $17.6 \pm 0.9$  kcal. mole<sup>-1</sup> and  $19.2 \pm 2.7$  kcal. mole<sup>-1</sup> were calculated for the production of cyanogen with TSX graphite and AGOT graphite, respectively. The production of hydrogen cyanide and carbon dioxide is ascribed to the presence of impurities in the nitrogen and graphite.

## Introduction

Recently, two studies of the reaction of dissociated gases with graphite have been reported.<sup>2</sup> Zinman investigated the reaction of carbon with a mixture of active nitrogen and hydrogen at 800° and found that hydrogen cyanide was the principal reaction product. In Giberson's study the graphite was maintained in the discharge region; paracyanogen was produced along with some hydrogen cyanide. In both investigations little care was taken in the outgassing of the graphite.

This study is the first in which the graphite was carefully outgassed and also the first in which the reaction was investigated as a function of the graphite temperature (1694 to 2365°K.). Cyanogen, hydrogen cyanide, and carbon dioxide were the products condensed in traps at liquid nitrogen temperature. The formation of hydrogen cyanide and carbon dioxide is shown to be due to impurities in the nitrogen and graphite.

## Experimental

Apparatus and Materials. In the apparatus used, the nitrogen was passed through two liquid nitrogencooled traps containing Molecular Sieve 4A,<sup>3</sup> a quartz tube containing copper turnings at 600°, and another Molecular Sieve trap at liquid nitrogen temperature. The gas then passed through a Manostat predictability flowmeter, a kerosene-cooled discharge tube, and a converging nozzle about 3 mm. in diameter, and impinged on the hot graphite surface at a distance of approximately 3 cm. from the nozzle (Fig. 1). The graphite was resistance heated by a.c. current passing through the water-cooled copper leads supporting the sample. The reactor was constructed from a 1500-cc. quartz bulb. Between the discharge tube and the inlet nozzle, provision was made for the introduction of nitric oxide through another Manostat flowmeter. The pumping system included a liquid nitrogen trap, an oil diffusion pump, and a mechanical fore pump. Products collected in four liquid nitrogen traps immediately following the reactor were transferred to a calibrated volume and then to Pyrex break-seals for analysis by a Perkin-Elmer vapor fractometer Model 154D equipped with thermistor and flame-ionization detectors and a silica gel column. In preliminary experiments the same amounts of products were collected with only two traps as with all four.

Pressure in the system was measured with either a Consolidated Electrodynamics Corp. Philips gage or a McLeod gage. The temperature of the graphite surface was measured with a Leeds and Northrup optical pyrometer, intercompared with one calibrated by the National Bureau of Standards. Temperature corrections were applied for the sight glass and for the deviation of the pyrometer from the 1948 temperature scale, but not for the emittance of the graphite. A Raytheon Microtherm Model CMD 4 unit (2450 Mc.) run at a setting of 110 watts was used to activate the nitrogen.

Samples of the specially purified nuclear grade graphites designated as TSX and AGOT<sup>4</sup> were obtained

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<sup>(2) (</sup>a) W. Zinman, Planetary Space Sci., 3, 46 (1961); (b) R. C. Giberson, HW-68380 UC-4, Chemistry, Office of Technical Services, Department of Commerce, Washington 25, D. C., 1961.

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GRAPHITE NOZZLE SIGHT TUBE

Figure 1. Schematic diagram of reactor.

from the National Carbon Company, Division of Union Carbide Corporation. The specially shaped sample (Fig. 1) had a front surface of about  $1.5 \times 1.0$  cm. and was mounted in the copper holder so that a beam of active nitrogen impinged on the center of the front surface of the graphite over an apparent area about 5 mm. in diameter. This area showed no temperature differences of more than  $5^{\circ}$ , while the ends of the front surface and the sides were at least 100° cooler.

The gases used were high-purity dry nitrogen obtained from the Linde Co. and nitric oxide from the Matheson Co. Hydrogen cyanide, prepared by the reaction of sodium cyanide and sulfuric acid, and Matheson cyanogen and "bone dry" carbon dioxide were used to calibrate the vapor fractometer. These three gases were trap-to-trap distilled before use; vapor fractometer analyses revealed no impurities.

Experimental Procedure. The system was evacuated to a pressure less than  $10^{-5}$  torr and the graphite degassed by heating to at least 2050° until the system pressure was again less than  $10^{-5}$  torr. Initial heating of the graphite vielded condensable products in the liquid nitrogen traps, but after using this degassing procedure, no detectable amount of product was collected in 1 hr. After starting the constant nitrogen flow, the temperature of the graphite was adjusted to that desired for the run and the discharge ignited. The collection period for reaction products started when the two traps nearest the reactor were simultaneously immersed in liquid nitrogen (the remaining traps were

immersed immediately following). At the end of the reaction period, the discharge was extinguished, the power to the sample terminated, and the graphite allowed to cool for approximately 10 min. with the nitrogen flowing. The system was isolated from the pumps and the condensable products transferred to the analytical manifold. The graphite was degassed in a similar manner before each run and the same piece of graphite was used repeatedly until visible erosion of the surface occurred.

The concentration of nitrogen atoms for a nitrogen flow of 0.0286 mole min.<sup>-1</sup> at 1.95 torr was estimated at the jet by titration with nitric oxide.<sup>5</sup> The titration was performed either before the reaction was initiated or after completion of the reaction. In several hourlong runs the nitrogen atom concentration did not change after the discharge had run approximately 2 min. Therefore, the discharge was initiated at least 5 min. before starting to collect products.

#### **Results and Discussion**

Preliminary experiments with molecular and active nitrogen showed a difference in the products collected in traps at liquid nitrogen temperature. Hydrogen cyanide and carbon dioxide were the only products collected from the reaction of molecular nitrogen and graphite, whereas in the case of the reaction of active nitrogen, cyanogen was also formed. The formation of hydrogen cyanide and carbon dioxide was a consequence, it is believed, of the presence of hydrogen, oxygen, and water impurities in the nitrogen. Indeed, direct addition of hydrogen to the nitrogen before activation increased the rate of hydrogen cyanide production by several orders of magnitude. In addition, it was found that the production of hydrogen cyanide and carbon dioxide decreased (but never quite to zero) when the nitrogen was purified before being allowed to react. The presence of small amounts of oxygen and hydrogen impurities in the nitrogen did not affect the rate of production of cyanogen.

In agreement with Stieber,<sup>6</sup> no significant amount of cyanogen was collected from the reaction with purified molecular nitrogen in the temperature range up to 2365°K. (TSX graphite: Table I). The limit of detection by vapor fractometer analysis was 10<sup>-8</sup> mole for cyanogen and hydrogen cyanide and  $10^{-7}$  mole for carbon dioxide. In contrast, easily detected amounts of





<sup>&</sup>quot;The Industrial Graphite Engineering Handbook," National (4)Carbon Company, Division of Union Carbide Corp., New York, N. Y.

P. Harteck, R. R. Reeves, and G. Mannella, J. Chem. Phys., (5)29. 608 (1958).

H. C. Stieber, unpublished communication in ref. 2a. (6)

cyanogen were found when active nitrogen was used (TSX: Table III; AGOT: Table IV). In a special check, the rate of formation of cyanogen was constant with time (Table II).

**Table I:** Products Collected in 30 min. from the Reactionof TSX Graphite and Purified Molecular Nitrogen<sup>a</sup>

| Temp.,<br>°K.                    | C2N2,<br>mole × 10 <sup>6</sup>    | HCN,<br>mole $\times$<br>10 <sup>6</sup> | CO2,<br>mole ×<br>10 <sup>6</sup> |
|----------------------------------|------------------------------------|--|-----------------------------------|
| 2212                             | <0.01                              | 0.05                                     | 0.24                              |
| 2365                             | Not detected                       | . 02                                     | .32                               |
| 2365                             | Not detected                       | . 01                                     | . 13                              |
| <sup><i>a</i></sup> $N_2 = 0.02$ | 86 mole min. <sup>-1</sup> ; $P =$ | 1.95 torr.                               |                                   |

 
 Table II:
 Time Dependence of the Products Collected from the Reaction of AGOT Graphite and Active Nitrogen at 2185°K.<sup>a</sup>

| Time,<br>min.  | $C_2N_2,$<br>mole $\times$<br>$10^6$ | $ m HCN$ , mole $	imes 10^6$          | $CO_2$ , mole $\times 10^6$    |  |
|--|--------------------------------------|---------------------------------------|--------------------------------|--|
| 5  | 0.32                                 | Not determined                        | Not determined                 |  |
| 15   | 0.91                                 | Not determined                        | Not determined                 |  |
| 30   | 2.06                                 | 0.43                                  | 0.61                           |  |
| $^{a} N_{2} = \min_{n=1}^{a} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{$ | 0.0286  mol<br>P = 1.95  to          | e min. <sup>1</sup> ; N atom =<br>rr. | = $0.0518 \times 10^{-3}$ mole |  |

The amounts of products collected from the reaction of active nitrogen with TSX and AGOT graphite were determined as a function of the graphite temperature and the nitrogen atom concentration (Tables III and



Figure 2. Arrhenius plot for the reaction of graphite and active nitrogen:  $\bigcirc$ , TSX;  $\square$ , AGOT.

IV). The corresponding activation energies and entropies for the production of cyanogen, calculated from the least square lines of Fig. 2, are  $17.6 \pm 0.9$  kcal. mole<sup>-1</sup> and  $-2.44 \pm 0.45$  cal. mole<sup>-1</sup> deg.<sup>-1</sup> for TSX and  $19.4 \pm 2.7$  kcal. mole<sup>-1</sup> and  $-3.03 \pm 1.26$  cal. mole<sup>-1</sup> deg.<sup>-1</sup> for AGOT.

| Table III : | Products Collected in 30 min. from the        |  |
|-------------|---|--|
| Reaction of | TSX Graphite and Active Nitrogen <sup>a</sup> |  |

|                | <b>C N</b> | HON        |          | N atom,       |                   |
|----------------|------------|------------|----------|---------------|-------------------|
| Tomp           | $C_2N_2$ , | HCN,       | $CO_2$   | mole          | C.N. /9N          |
| °K.            | 106        | 104        | 106      | $\times 10^3$ | × 10 <sup>2</sup> |
|                |            |            | 0.04     |               | <u> </u>          |
| 1694           | 1.34       | 0.12       | 0.24     | 0.0539        | 0.41              |
| 1694           | 1.46       | . 27       | .41      | .0539         | . 45              |
| 1800           | 1.64       | . 22       | . 46     | .0518         | . 53              |
| 1853           | 1.85       | . 12       | 1.13     | .0580         | . 53              |
| 1853           | 1.88       | .12        | 0.25     | .0539         | . 58              |
| 1907           | 1.85       | . 07       | 0.52     | .0518         | . 60              |
| 1907           | 2.25       | . 03       | 1.16     | .0518         | .72               |
| 1963           | 2.13       | . 40       | 1.14     | .0518         | . 69              |
| 1963           | 2.36       | . 10       | 0.41     | .0518         | .76               |
| 1973           | 2.53       | .03        | . 29     | .0539         | .78               |
| 2020           | 2.74       | . 33       | . 50     | .0518         | .88               |
| 2020           | 2.42       | . 01       | 1.08     | .0394         | 1.02              |
| 2058           | 2.83       | . 13       | 0.31     | .0456         | 1.03              |
| 2058           | 3.97       | . 03       | . 33     | .0539         | 1.23              |
| 2068           | 3.69       | .15        | .34      | . 0539        | 1.14              |
| 2109           | 3.22       | . 29       | . 28     | .0539         | 1.00              |
| 2109           | 3.54       | .13        | . 14     | .0518         | 1.14              |
| 2160           | 3.28       | . 20       | . 21     | .0518         | 1.06              |
| 2212           | 3.74       | . 26       | .47      | .0456         | 1.37              |
| 2212           | 4.86       |            | . 26     | .0580         | 1.40              |
| 2263           | 4.61       | .17        | . 19     | .0539         | 1.43              |
| 2314           | 4.98       | . 17       | . 25     | .0518         | 1.60              |
| 2365           | 5.24       | . 18       | . 24     | .0518         | 1.69              |
| $^{a} N_{2} =$ | 0.0286 mol | e min. ~1; | P = 1.95 | torr.         |                   |

| Table IV:   | Products Collected in 30 min. from t | he |
|-------------|--------------------------------------|----|
| Reaction of | AGOT Graphite and Active Nitrogen    | a  |

| °K   | C2N2,<br>mole ×<br>106 | HCN,<br>mole X | $CO_2$ ,<br>mole $\times$ | N atom,<br>mole<br>min. <sup>-1</sup> | $C_2N_2/2N$ |
|------|------------------------|----------------|---------------------------|---------------------------------------|-------------|
| 11.  | 10-                    | 10-            | 10.                       | × 10*                                 | X 10*       |
| 2031 | 1.40                   | 0.37           | 0.43                      | 0.0518                                | 0.45        |
| 2050 | 1.72                   | . 52           | .71                       | .0601                                 | . 48        |
| 2083 | 1.89                   | . 45           | .70                       | .0643                                 | . 49        |
| 2108 | 1.51                   | . 32           | .68                       | .0518                                 | . 49        |
| 2134 | 1.75                   | . 41           | . 61                      | . 0540                                | . 54        |
| 2185 | 2.06                   | . 43           | . 61                      | .0518                                 | . 66        |
| 2237 | 2.41                   | . 48           | .72                       | .0580                                 | . 69        |

41

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## Anhydrous Perchloric Acid: Heat Capacities and

## Thermodynamic Functions from 5 to 300°K.

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The thermal behavior of anhydrous perchloric acid was studied by adiabatic calorimetry and the data obtained were used as the basis for the evaluation of the thermodynamic functions. The triple point of perchloric acid occurs at 172.0°K. with an associated entropy of melting of 9.67 cal./(mole °K.). At 298.15°K. the values of the heat capacity at constant pressure  $(C_p)$ , the practical entropy (S°), the enthalpy function  $[(H^\circ - H_0^\circ)/T]$ , and the Gibbs free energy function  $[(F^\circ - H_0^\circ)/T]$  are 28.80, 45.02, 23.11, and -21.91cal./(mole °K.). The fusion data conflict with the phase diagram reported by others and provide evidence that HClO<sub>4</sub> does exist as an independent species in the crystalline state. This conclusion is consistent with that obtained from recent infrared and Raman spectra of the solid which reveal bands similar to those of the liquid.

## Introduction

Although anhydrous perchloric acid is notorious primarily as a consequence of its marked instability, methods for its preparation were described as early as  $1818,^2$  and liquid nitrogen temperatures may be used to retard decomposition.<sup>3</sup> Several investigators<sup>4-7</sup> have examined its physical properties but few thermal and thermochemical data are available.<sup>8</sup> Interest in the properties of anhydrous perchloric acid evolved from consideration of the thermodynamics of the hydronium perchlorate (perchloric acid monohydrate) transition. This paper is the first in an endeavor to study the system chlorine heptaoxide-water.

## Experimental

Anhydrous Perchloric Acid Sample. The sample for calorimetric investigation was prepared by the method of Smith,<sup>3</sup> with rigorous observation of two precautions: complete exclusion of oxidizable materials including vapor as well as condensed phase contaminants, and adequate temperature control of the distillation reservoir and other portions of the apparatus where perchloric acid vapors are present. Even the pure va-

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