Mellitic Acid from the Oxidation of Graphite with 90% Nitric Acid

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SEVERAL METHODS utilizing nitric acid for the processing of graphite-matrix nuclear reactor fuels have been studied (*1, 2, 5*). Generally, 4 to 15*M* HNO_3 is employed; however, in one of these procedures (*2*) the fuel is simultaneously disintegrated and leached with boiling 90% HNO_3. Prior studies (*3, 7, 9*) showed that soluble species such as oxalic and mellitic (benzene hexacarboxylic) acids were produced in the oxidation of graphites with various aqueous reagents. The object of the present study was to determine the products formed in the oxidation, with 90% HNO_3, of a nuclear grade graphite (Type GBF) and to obtain a rough measure of the rate of oxidation.

RESULTS

Type GBF graphite oxidized very slowly in boiling 90% HNO_3. Less than 70% was oxidized in digestion periods of up to 475 hours, even though the samples disintegrated to fine powders during digestion (Table I). In all experiments, less than 6% of the graphite that had been oxidized was converted to soluble species, indicating that the main reaction product was CO_2. The unreacted graphite, after thorough water-washing, analyzed 98 to 99% carbon.

The red-brown to yellow soluble species were mixtures of polyfunctional aromatic acids having equivalent weights in the range of 60 to 90 grams/equiv. (Table II). Melting points, greater than 250° C., and infrared spectra, showing strong peaks for the $C=O$ and OH groups with little C—H, C—N, or N—O bonding, indicated that the mixtures consisted of aromatic acids with little or no nitration. Infrared evidence of C—O—C bonding suggested that ether and/or ester groups were also present. The low nitrogen content (less than 0.5%) of the mixtures further supports the infrared analyses.

The main component of the mixtures was mellitic acid. Based on the weights of the insoluble ammonium salt, mixtures from runs lasting 200 hours or more contained 60 to 80% mellitic acid (Table III). However, based on equivalent weights, the mellitic acid content of the mixtures from runs 4 and 6 could have been as high as 91 to 96%. The amounts of solids from the shorter runs were insufficient to allow estimation of the mellitic acid content.

Mellitic acid was the only benzenoid acid detected in the mixtures. Paper (*4*) and partition (*6*) chromatography experiments showed that none of the benzene acids containing 1 to 4 carboxyl groups was present. No benzene pentacarboxylic acid was found by comparing the x-ray powder patterns of the mixtures with that of the benzene pentacarboxylic acid standard. The presence of several aliphatic mono- and dicarboxylic acids could also have been detected by the partition chromatographic technique used (*8*); however, none was found.

Oxalic acid could not be detected in the mixtures by x-ray analysis or by subjecting the mixtures to high vacuum at 110° C.

The results obtained in this study support Juettner's (*7*) finding that mellitic acid is the chief constituent of the soluble species formed in the nitric acid oxidation of graphite. No oxalic acid was formed, although it is produced in the alkaline permanganate oxidation. High molecular weight intermediates, as suggested by Juettner, are undoubtedly formed as evidenced by the high equivalent weights of the products from the short oxidation runs (Table II). The decrease in equivalent weight with oxidation time is to be expected as the intermediates are oxidized to mellitic acid.

EXPERIMENTAL

Graphite Oxidation. Samples of National Carbon Co. grade GBF graphite (ash content, less than 0.007%; boron content, less than 0.2%) were refluxed with 90% HNO_3 (Baker and Adamson reagent grade, Sp. Gr. at 15° C., 1.49-1.5) for predetermined times. When the reaction lasted longer than 100 hours, the volume was kept constant by periodic addition of fresh acid. During the digestions, the temperature rose from 90° C., the approximate boiling point of 90% HNO_3, to about 120° C. After the digestion period, the nitric acid solution was removed by vacuum filtration and the unoxidized graphite was washed thoroughly with water to remove residual solution. The residual graphite was dried, weighed, and analyzed for carbon to determine the extent of oxidation. The nitric acid and wash solutions were evaporated to dryness at temperatures below 40° C. to obtain the organic acid mixtures. The mixtures were dried at 105 to 110° C. to reduce the water content to less than 5%. The equivalent weights of the mixtures, and of the acids prepared during the course of this study, were determined by potentiometric titration.

Determination of Mellitic Acid Content. Samples of the mixtures were digested with an excess of boiling concentrated NH_4OH for 16 to 20 hours. The system was then cooled to about 0° C., maintained there for at least an hour, and the ammonium mellitate recovered by vacuum filtration. The ammonium mellitate was washed with cold

Table I. Effect of Time on the Oxidation of Type GBF Graphite with Boiling 90% HNO_3

Run No.	Reaction Time, (Hr.)	Initial State of the Graphite Samples	Total Amount of Graphite Oxidized, (%)	Amount of Graphite Oxidized to Soluble Products, (%)
1	50	-100 mesh powder	1.6	0.065
2	66.5	-100 mesh powder	3	. . .
3	100	-100 mesh powder	2.3	0.12
4	212	1-inch cubes	69	5.8
6	475	1-inch cubes	56	3.0

Table II. Results of Analysis of Products of Graphite-HNO_3 Reactions

Run No.	Analyses of Soluble Products			
	%, Carbon	%, Hydrogen	%, Nitrogen	Eq. Wt., (G./Eq.)
1	27.6	1.5	...	89.0
3	36.4	2.2	...	87.6
4	41.5	2.0	0.5	62.7
6	41.8	1.8	0.26	59.2

Table III. Mellitic Acid Yields from Graphite-HNO_3 Reactions

Run No.	Amount of Mellitic Acid in Soluble Products, (%)	Analyses of Ammonium Mellitate,[a] (%)		
		C	H	N
4	56.7, 63.7	33.0	5.2	18.2
5	57	31.7	5.2	17.2
6	77	32.1	5.6	19.4
Calculated for pure ammonium mellitate:		32.4	5.44	18.9

[a] Anhydrous, dried at 105° to 110° C.

concentrated NH_4OH before being dried at 105° to 110° C. Losses were probably less than 10% since the solubility of ammonium mellitate in concentrated NH_4OH at 0° C. is only about 0.002 gram/liter. The ammonium mellitate was essentially pure and anhydrous (Table III).

Paper Chromatographic Studies. The procedure used was identical to that described by Clingman and Sutton (*4*).

Partition Chromatographic Studies. These tests were conducted using a modification of Fishwick's (*6*) procedure to confirm the results obtained with the paper chromatographic method. The support was J.T. Baker Chemical Co. 80 to 200 mesh silica gel (suitable for chromatographic use) which was dried three hours at 105° to 110° C. before use. The gel (20 grams) was mixed with 5 ml. of $0.5N$ H_2SO_4 (the stationary phase) before being transferred to the chromatographic tube with chloroform. The chromatographic tube was a 100-ml. Pyrex buret, 1.5 cm. I.D., fitted with a Teflon stopcock. The eluting solvents, solutions of butanol and chloroform, were prepared from reagent grade materials. The elution program was the same as that used by Fishwick; however, with the silica gel used in this work, elution of benzene pentacarboxylic acid and mellitic acid could not be achieved. The lower benzene acids eluted nicely and yielded about the same peak effluent volumes as reported by Fishwick.

Acids Used as Standards for the Chromatographic Studies. Oxalic acid dihydrate: Baker and Adamson reagent grade. Benzoic acid: Baker's Analyzed reagent. *o*-Phthalic acid: Eastman Organic Chemicals. Trimellitic acid: prepared from Amoco Chemical Corp., trimellitic anhydride by heating in distilled water, then cooling to precipitate the free acid. Equiv. wt.: Calcd., 70.0; Found, 71.3. Pyromellitic (1, 2, 4, 5-benzene tetracarboxylic) acid: Eastman Organic Chemicals practical grade (greater than 90%). *Anal.* Calcd., C, 47.2; H, 2.38; Equiv. wt., 63.5; Found, C, 46.9; H, 2.4; Equiv. wt., 64.2. Benzene pentacarboxylic acid: prepared by the alkaline permanganate oxidation of pentamethyl benzene (Eastman) following the procedure given by Fishwick (*6*). The yields obtained, 10 to 15% were much lower than those reported by Fishwick. *Anal.* Calcd., C, 44.3; H, 2.0; Equiv. wt., 59.6; Found, C, 43.1, 43.9, 44.2; H, 2.1, 2.07; Equiv. wt., 59.5, 59.8. Mellitic acid: recovered from run 6 by adding lead acetate to a solution of the ammonium salt to precipitate the lead salt; bubbling H_2S through a slurry of the lead salt to generate the free acid; then recrystallizing from 70% HNO_3. *Anal.* Calcd., C, 42.1; H, 1.77; Equiv. wt., 57.0; Found, C, 41.9; H, 1.7; Equiv. wt., 57.5.

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