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TITLE: **CHEMISTRY OF DETONATION SOOT: DIAMONDS, GRAPHITE, AND VOLATILES**

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CHEMISTRY OF DETONATION SOOT: DIAMONDS, GRAPHITE, AND VOLATILES

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Detonation of a number of pure and composite explosives in tanks filled with Ar gas have yielded solid carbonaceous products (soots) with a rich chemistry. Although there are similarities, the soot from each explosive has some uniqueness. The soots are composed of very small solid particles of graphite and often diamond, having characteristic dimensions of about 20 atomic diameters. This small size and the presence of a 25 wt % heat-labile component implies an important surface chemistry for these soots. The heat-labile compounds may give clues about the structure, the surface chemistry, and the mechanism of soot formation.

INTRODUCTION

Detailed knowledge of the chemical kinetics and equilibria of detonation have long been a desired, but elusive, goal. One focus of this chemistry is the coagulation of carbonaceous solid (soot) from carbon initially present as the skeletal atoms of small organic CHNO molecules. Current detonation models[1] predict that the oxygen reacts first to form H_2O from the available hydrogen, then the remainder reacts with carbon to form CO_2. Any carbon left over forms the soot. (The nitrogen forms N_2.) The nature of this soot and the details of its formation have been the subject of much discussion.[2] The literature on non-detonation soots is extensive, and numerous soot types have been described.[3-5] However, reports on the chemical composition and structure of detonation soot are just beginning to appear.[6,7]

The characteristic dimensions of the basic soot particles observed,[6] both diamond and graphite, are on the order of 20 interatomic bond lengths. These are smaller than the maximum size permitted by an agglomeration process limited only by diffusion in the dense detonation products.[8] The graphite particles are not balls of small polynuclear aromatic hydrocarbon (PAH) crystals, as in hydrocarbon combustion soot.[3] Instead, they are ribbons resembling carbon blacks graphitized at high temperature.[3,5,9] Because of this similarity to carbon blacks, it seems plausible that the growth processes may be similar. Furthermore, a rapidly quenched mixture containing these graphite ribbons might scavenge soot-growth intermediates[10] and other chemical species in the detonating explosive, including reaction intermediates and stable products, which might give clues about the soot-formation chemistry. These considerations led us to investigate possible heat-labile surface components of the soots.

Earlier work on detonation products established that the soots contain some nitrogen, hydrogen, and probably oxygen, in addition to the largest component, carbon.[11,12] From detonation calorimeter data one could deduce a positive heat of formation for the soot.[12] The bonding of the noncarbon atoms in the soot had not been established. Here we will review briefly pertinent previous data, report further work on soot diamond, and present new findings on a large variety of thermally labile molecules found in the soot. These results suggest possible chemical structures in the detonation soot, give support to a restricted diffusion model of solid carbonaceous cluster formation, and suggest a way to estimate the heat of formation of the soot from its components.

EXPERIMENTAL

Some of the soot samples in this study came from explosive charges fired at the Fraunhofer-Institut für Chemische Technologie (ICT) in the Federal Republic of Germany, and others came from the Los Alamos National Laboratory.

The following came from ICT: Samples #27/30 and #28/30 were pure cast TNT. Composite explosives were cast from molten TNT mixed with 59.5 wt % powdered cyclotrimethylene-trinitramine (RDX) to make samples #27 and #34/30; 50 wt % powdered triaminotrinitrobenzene (TATB) to make sample #60; 50 wt % powdered nitroguanidine (NIGU) to make samples #63, #55/20, and #10/41; and 50 wt % powdered ammonium nitrate (AN) to make sample #36.

The charges were in the form of (nominally) 300-g cylinders 50 mm diam × 100 mm long. They were boosted by a 15-g pellet of RDX and were fired in a 1.5 m^3 tank filled with 1 atmosphere of Ar gas, except for sample #10/41, which was fired in vacuum. A few minutes after firing, the Ar was replaced with air and the soot was swept from the tank into sample bottles. Samples were dried at 105°C to constant weight. Elemental analyses[11] and initial results[12] from samples #27, #60, and #63 have been published.

The following samples were from Los Alamos: Sample #H1057 was pure TNT pressed to a density of 1.470 g/cm^3, sample #H1017 was pure TNT pressed to a density of 1.630 g/cm^3, sample #H1058 was pure TATB pressed to near crystal density, and sample #H1059 was pure RDX pressed to near crystal density. These charges were cylindrical, 50 mm diam × 100 mm long, and were boosted with a 15-g charge of RDX. The Los Alamos charges were fired in a steel sphere 6 ft (1.83 m) in diameter, with a volume of 3.0 m^3 filled with 760 torr (1 atm) of Ar gas. The soots were collected and dried as described above.

The micromorphologies of the soots were recorded by transmission electron microscopy (TEM), and crystal structures were determined by transmission electron microscope electron diffraction (TEMED).[6] The diamonds were isolated by oxidative removal of the other soot components with HNO_3 and $HClO_4$ (Reference 6). Diamond in the residue was identified by x-ray diffraction (XRD) powder patterns. Measurements with an x-ray diffractometer determined the diameters of the recovered diamonds and confirmed the diamond lattice spacings. Thermally labile components in the soot were weighed by thermogravimetric analysis (TGA) and were identified with direct insertion probe (DIP) mass spectrometry.

ANALYSIS OF RAW SOOTS

TEM examination of samples #27, #60, and #63 has shown that the soots are composed of graphite ribbons having a smallest dimension of 3 nm and diamonds having diameters of 3-7 nm (Figure 1 and Reference 6). The interplanar spacings measured by TEMED from a group of the diamonds in sample #27 agree well with the spacings of bulk diamond (Table I and Reference 6).

The detonation graphite appears as partially graphitized (turbostratic structure by TEMED) ribbons a few nm thick, not as aggregated smaller particles or crystals. This observation contrasts with the reported structures of graphitic soots from hydrocarbon flames, which are typically spheres 10-500 nm in diameter, composed of many small graphitic crystallites less than about 1 nm thick.[3] The detonation diamond appears to

TABLE I. DIAMOND STRUCTURE

	TNT/RDX #27	TNT/TATB #60	TNT/NIGU #63
Wt % in soot	16	24	24
Diameters, nm			
TEM image	7	3	3
XRD, diffractometer	4.5	2.8	2.8
Spacings (TEMED), nm			
(111)	0.2058		
(220)	0.1266		
(311)	0.1075		
(400)	0.0884		
(440)	0.0636		
Spacings (XRD Diff), nm			
(111)	0.206	0.206	0.206
(220)	0.126	0.126	0.126
(311)	0.108	0.108	0.108

FIGURE 1. TEM MICROGRAPH OF THE SOOT FROM SAMPLE #27 (TNT/RDX). D DENOTES DIAMOND STRUCTURES AND T THE TURBOSTRATIC GRAPHITE RIBBONS. THE BAR SCALE SHOWS 10 NM, WHICH IS ABOUT 70 INTERATOMIC COVALENT BOND LENGTHS IN DIAMOND OR GRAPHITE.


T
D
10 nm
40 TNT, 60 RD

be almost perfect single crystals, rather than aggregates of smaller crystals. We have found no evidence for "rolled chickenwire" structures of the buckminsterfullerene family.[13] Furthermore, the sizes of the diamond and graphite particles observed in these detonations appear to be too small for unrestricted growth by aggregation.

A model for growth of detonation soot by diffusion-controlled aggregation has been developed by Shaw and Johnson (SJ).[2] We can apply the SJ model to these detonations with the aid of a hydrodynamic model for the expansion of the detonation products.[14] A large portion of the explosive charge is maintained near the detonation density for about 3×10^{-6} s, whereas the characteristic time for the unrestricted aggregation of solid carbon in the SJ model is 2×10^{-12} s. The growth time divided by the characteristic time gives the number of atoms in the most probable particle size, in our case 1.5×10^6 atoms. A crystalline diamond sphere this size would be 26 nm in diameter, whereas we see a 7-nm maximum, too small in volume by a factor of 50.

The differences suggest that (1) particle growth has additional restrictions and (2) either aggregation progresses in increments closer in size to atoms than to small crystals or the final aggregates are annealed well enough to obscure component crystallites, but, in the case of graphite, not well enough to accomplish extensive graphitization. The small size of the diamonds and the graphite ribbons raise the possibility that surface chemistry may influence their relative stabilities,[15] their heats of formation, and possibly their growth mechanisms.

Gouy-balance measurements on the raw soot show evidence of unpaired electrons, a common feature of finely divided solid carbons. Elemental analysis of the dry soots shows the presence of a few atom % each of H, N, and O atoms in addition to C atoms, and TGA analysis shows that about 25% of the soot is heat-labile (Figure 2). The section below on volatiles lists some of the probable heat-labile components, which give an idea of the functional group chemistry of the soots.

DIAMOND RESIDUES

Diamond structures were found in the TEM images,[6] and the presence of diamond was confirmed by strong x-ray powder patterns in the oxidation residues of samples #27, #60, and #63. The oxidation residue from sample #34/30 (60% RDX/40% TNT, the same as sample #27) also shows a strong powder pattern of 5-nm-diam diamond. However, the soots from the pure explosives from both ICT and Los Alamos yield only small amounts of residue after oxidation, and the residues show only weak diamond x-ray powder patterns. This result agrees with Soviet results, where they find that a 50/50 mixture of TNT and RDX produces more diamond than pure TNT.[7]

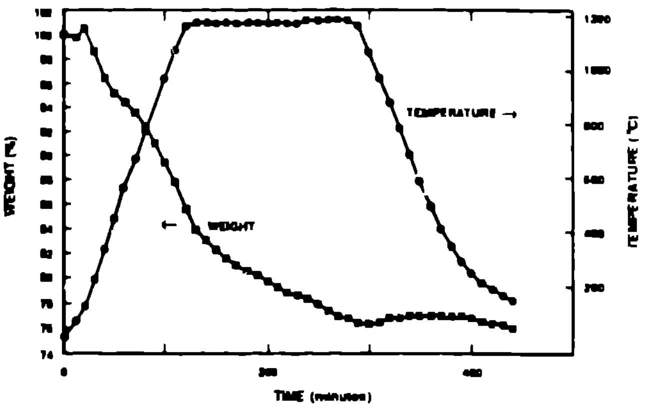

FIGURE 2. TGA OF RAW SOOT SAMPLE #27/30 (PURE TNT) IN 1 ATM OF HE GAS. THERE IS ABOUT 5% WEIGHT LOSS AT 350°C, THE UPPER LIMIT OF THE DIP GAS ANALYSES, AND ABOUT 25% AT THE TERMINATION OF THE RUN AT 1200°C AFTER 300 MIN.

The diameters of the diamonds in the oxidation residues showing strong diamond powder patterns were determined by the widths of their diffraction lines measured on an x-ray diffractometer, and in all three cases, they are nearly equal to the diameter of the diamonds observed in the TEM images (Table I), implying that the diamonds are single crystals.

No measurable residue was obtained from sample #10/41 (TNT/NIGU), which was fired in a vacuum. This result can be compared to that of sample #63 (also TNT/NIGU, but fired in 1 atm of Ar), where diamond residue is 24 wt % of the soot. Sample #10/41 obviously underwent reshock at the vessel wall; evidently the diamonds do not survive this process. The residue from sample #36 (TNT/AN) also contained no diamonds.

Auger/ESCA analysis shows that the diamond residue from sample #63 has some O and N atoms, which are probably on the surface, because they are largely removed by surface sputtering.

VOLATILES

DIP mass spectrometry of raw soots (with the temperature ramped at 20°C/min up to 350°C) typically shows the sequence H_2O, CO, CO_2, NH_3, HNCO, HCN, and HCl as major volatiles. Patterns attributable to a variety of organics generally starts at ca. 150°C. A prominent peak at 60 atomic mass units (AMU) suggests the presence of urea. In the case of sample #10/41 (TNT/NIGU) the pattern of (undecomposed) NIGU is present. Sample #55/20 (TNT/NIGU) releases a short burst of gas at about 240°C that fits the empirical formula $(HNO)_x$. The DIP results from sample #27/30 (pure TNT) show clearly a number of peaks consistent with a sequence of fused aromatic ring compounds, similar to soot precursors in other chemical systems,[4] but here with occasional -CN group substitution (Figure 3). Identifications were aided by comparison with known samples run in the DIP and with published spectra.[16,17]

Diamond isolated from sample #63 gives off H_2O at low temperatures and a CO_2-CO mixture starting at ca. 300°C, which suggests that the diamond recovered by acid oxidation may have a carboxylated surface. No significant nitrogen-containing species were driven off.

CONCLUSIONS

These results show that the soot has a rich chemistry involving heteroatoms. Heat-labile components, containing a variety of chemical species, have been found in quantities comparable to the number of surface atoms on the solids. The results from the possible soot precursors suggest that -CN groups may be present as surface terminators.

These initial investigations suggest a way to characterize the chemical structure of detonation soot, which might permit estimates of the heat of soot formation and give important clues about possible mechanisms of soot formation. If the various methods outlined above can be made sufficiently quantitative, bounds can be put on the heat of soot formation. The interiors of the diamonds are crystallographically the same as bulk diamond, the graphite appears to be a recognized form, and the volatiles are all known molecules. The principal unknowns are the surface contributions of the diamond and graphite, which could be considerable because of the large specific areas. Further challenges are understanding the kinetics of the soot formation and the binding of the adsorbed species to the surfaces.

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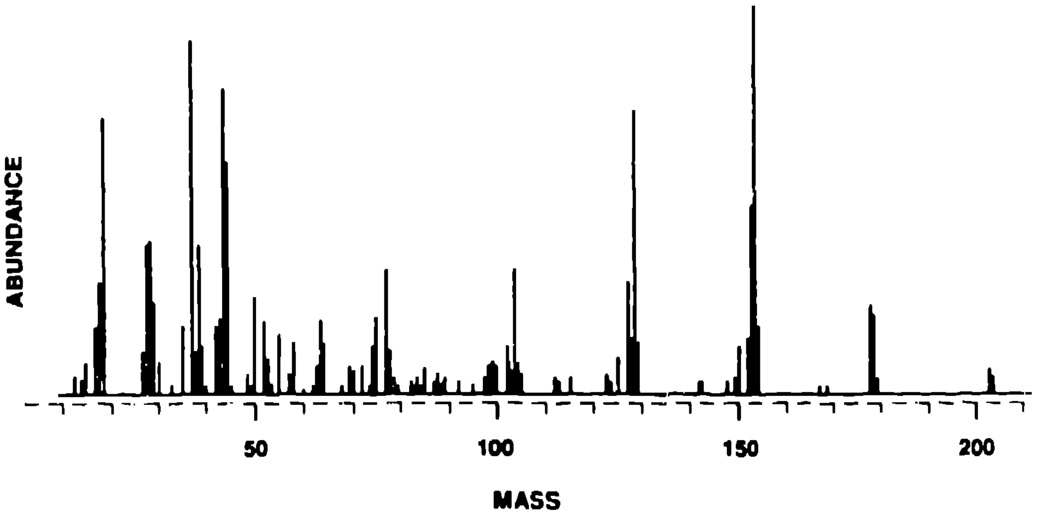

FIGURE 3. DIP MASS SPECTRUM FROM SAMPLE #27/30 (PURE TNT). THE TIME EVOLUTION OF THE MAJOR PEAKS SEEN IN THIS SPECTRUM (AMU OF PRINCIPAL PEAKS IN PARENTHESES) ARE CONSISTENT WITH THE PRESENCE OF NH_3 (17,16), H_2O (18), HCN (27), CO (28), NO (30), HCL (36), HNCO (43), CO_2 (44), BENZONITRILE (103), NAPHTHALENE/BENZENEDICARBONITRILE (128), ACENAPHTHALENE/BIPHENYLENE (152), NAPHTHALENECARBONITRILE (153), PHENANTHRENE/ANTHRACENE (178), PYRENE/FLUORANTHENE (202), AND ANTHRACENECARBONITRILE (203).

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