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Informal Progress Report of the Explosives Group September-November 1958

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Lawrence Livermore National Laboratory

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Informal Progress Report of the Explosives Group of the Lawrence Radiation Laboratory for September, October and November 1958.

DECLASSIFICATION STAMP ON REVERSE.

Compiled by: John Kury
January 7, 1959

DETONATION STUDIES

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A. General

The relatively high heats of combustion of CHN compounds containing multiple bonds has prompted an investigation of the possible use of these compounds as explosives components. Three possible systems are being considered for testing in the small scale plate push apparatus: acrylonitrile-tetranitromethane, propiolonitrile-tetranitromethane and dicyanoacetylene-tetranitromethane. Samples of propiolamide and acetylene dicarboxamide, intermediates in the synthesis of propiolonitrile and dicyanoacetylene respectively, have been prepared and their infrared spectra determined.

A small scale "plate push" experiment was performed with a 17.8 weight % solution of acrylonitrile in tetranitromethane (CO_2 balanced). This solution at a density of 1.39 gm/cc gave a plate push energy per gram (Ep) relative to TNT of 1.41. Similar experiments previously reported on solutions of ethyldecaborane in tetranitromethane (ρ = 1.44 gm/cc, balanced to CO_2) and nitromethane in tetranitromethane (ρ = 1.32 gm/cc, balanced to CO_2) gave Ep values of 1.41 and 1.39 respectively. These values are in agreement with recent Los Alamos hydrodynamic-thermodynamic calculations indicating approximately equal Chapman-Jouguet pressures of 180 kbars for the above explosives.

A sample of propiolonitrile (cyanoacetylene) has been prepared by dehydration of propiolamide. This material has been shown to be miscible with tetranitromethane at room temperature over the range of interest for plate push experiments. After storage of a CO-balanced mixture at ~ 25° for 20hrs., 98% of the propilonitrile was recovered by a simple pot to pot distillation on a vacuum line. Infrared spectra of the two separated components showed no evidence of reaction. The mixtures did not appear to be extremely shock sensitive.

A small sample of dicyanoacetylene has been prepared and its compatibility with tetranitromethane is being determined.

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DETONATION STUDIES - Cont'd.

B. Calorimetry

A series of measurements of the heat of explosion of uncased charges of bis-trinitroethylnitramine (BTNEN) has been performed. The derived value of ΔE is about -1360 cal/gram (water liquid), compared with a theoretical of -1344. A similar series with PETN gives a value of -1500, compared with -1548 calculated both for the "idealized" reaction and the approximate actual overall reaction as determined by analysis of the products.

These experiments were performed using platinum bridge wire detonators loaded with the same explosive as that comprising the main charge--construction materials being gold and ceramic. The same system with tetryl does not perform. A detonating system for this explosive is now being developed.

A satisfactory detonator system for tetryl has been developed and measurements of heats of explosion of this compound are now in progress. A preliminary value of 920 cal/gm was determined for the ΔE of explosion from several 0.340" diameter unconfined charges ($\rho = 1.69$ gm/cc.)

C. Microwave Studies

A program to investigate some properties of high explosives at microwave frequencies, about one centimeter wavelength, is being undertaken.

The fact that the detonation front is a region of ionization of fairly high density implies that for wavelengths longer than some critical value the detonation front will be opaque and therefore a good reflector. Making this reflecting surface one arm of a microwave interferometer will allow absolute determinations of the detonation velocity of the high explosive.

By calibration of the output voltage of the interferometer versus displacement of a thin metal plate at the front surface of the high explosive, free-surface velocities and therefore Chapman-Jouguet pressures can be obtained.

Finally, by making the assumption that the detonation front is a region in thermodynamic equilibrium and should therefore radiate as a black body, a measurement of the microwave noise will give a value for the effective temperature of the detonation front.

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DETONATION STUDIES - Cont'd.

D. Heterogeneous Explosives

To better understand the energy release of metal-loaded organic explosives, a series of experiments has been started using bis-trinitroethylnitramine (BTNEN), trinitroacetamide (TNAA), and mixtures of BTNEN and TNAA as the organic matrices (TNAA, as yet unsynthesized, has the same empirical formula as BTNEN).

Hydrodynamic-thermodynamic IBM 704 calculations indicate that these oxygen-rich explosives, even though differing as much as 30% in energy release, have the same detonation products, only moderately different detonation pressures, and considerably different detonation temperatures. Samples of Al, Al_2O_3, Mg, MgO, B, B_2O_3, C and Cu in two particle size ranges (1 to 10μ and 50-70μ) have been prepared and the detonation velocity, "plate-push" energy release and calorimetric energy release of mixtures of these with the above organic explosive are being investigated.

SYNTHETIC CHEMISTRY

A. Nitrogen-Fluorine Compounds

A high voltage discharge apparatus containing a quartz window in the discharge tube was assembled on the emission spectrograph to determine if any NF_2 or NF radicals were formed in the discharge through NF_3. The range from 2200Å to 9000Å was examined. Only molecular nitrogen and atomic fluorine were observed. A small amount of oxygen was observed, probably coming from the reaction of fluorine with SiO_2. SiF_4 was found in the traps beyond the discharge, but no SiF emission bands were observed in the discharge.

Nitrogen trifluoride chemistry was continued in a brief examination of its reaction with lithium hydride. NF_3 at 2 to 5 mm was passed through a 2 1/2 x 1/2 inch bed of 60-100 mesh lithium hydride. Reaction was first observed at 400°C. Mass spectrograph analysis of the volatile products showed the presence of only N_2, NO, NO_2 and the initial NF_3; the oxygen presumably came from lithium oxide impurity.

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SYNTHETIC CHEMISTRY - Cont'd.

Exploratory work was done on the reaction of NF_3 and C_2H_2 in the presence of hot copper turnings. The mixture of NF_3 and C_2H_2 at about 5 mm pressure was passed with pumping through a 2 1/2" x 3/8" bed of copper turnings at temperatures from 225° to 500°C. The products retained in a -196°C trap were analyzed by chromatography and mass spectrometry. There were small traces of fluorinated hydrocarbons produced, but the principle products were the starting materials and N_2F_4. The yield of N_2F_4 increased at the higher temperatures.

In another attempt to introduce NF_2 radicals into molecules, NF_3 plus H_2 were passed over copper at 400°C. The only volatile product besides the starting materials was N_2F_4, and no HNF_2 was found. Similar results were found when ammonia was used instead of hydrogen.

Several attempts were made to synthesize N_2F_4 by reaction of NF_3 with copper at elevated temperature according to a method recently reported in the literature. Only a few seconds contact time were found necessary at 375°C with fresh copper, but as the copper was aged much longer residence times and/or higher temperatures were necessary.

The reaction of NF_3 with excess sodium in liquid NH_3 at -40° has been investigated; if N_2 and NaF were produced quantitatively, the reaction might be used calorimetrically to determine the heat of formation of NF_3. In each of two trials, about one-sixth mole of N_2 was produced from each mole of NF_3; no unreacted NF_3 remained. The solid residues remaining after evaporation of the solution from the first trial were hydrolyzed; fluoride was determined and found to correspond approximately quantitatively with NF_3 used.

B. Boron-Hydrogen-Nitrogen Compounds

The mixture of pentaborane with hydrazine is reported by the Olin Matheson Co. to have promise as a high energy propellant. Boron nitride and hydrogen are presumed to be the reaction products:

$$2\ B_5H_9 + 5\ N_2H_4 = 10\ BN + 19\ H_2$$

This, or a similar system, may also be of interest as an explosive. An attempt to mix B_5H_9 and N_2H_4 in the laboratory on a mg. scale did result in a violent explosion.

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SYNTHETIC CHEMISTRY - Cont'd.

Another example of such a system is diborane-hydrazine. Using conventional bond energy tables (UCRL 3428) to calculate the heat of formation of the solid adduct of diborane and hydrazine, $H_3B\text{-}NH_2\text{-}NH_2\text{-}BH_3$, one obtains an energy of explosion of ~ 3 Kcal/gm for this material assuming boron nitride (solid) and hydrogen (gas) as products. The volume of gas produced per gram on this basis is also quite high, approximately 1.9 ℓ/gm. However all attempts to effect a detonation in this material on a conventional impact machine (drop hammer) and in a plate-dent test have so far failed.

In the investigation of hydrazine-borane systems combinations of hydrazine with diborane, pentaborane-9, and ethyldecaborane have been examined.

The hydrazine-diborane, $B_2H_6 \cdot N_2H_4$, formed at -80° was found to be unstable at room temperature. The material was found to lose nearly half of its hydrogen in a few hours, finally forming a crystalline product with a well-defined X-ray diffraction pattern. This solid product could not be detonated, however, either with the drop hammer or by the PETN detonator-booster used in the plate dent test. At 300°C in vacuum the solid decomposes smoothly to another solid material which is amorphous.

Pentaborane and hydrazine were combined without an explosion by using diethyl ether as a solvent. The resulting solid product after removal of the ether could not be detonated on the drop hammer at 160 cm with a 5 Kg weight, but the failure may have been due to air damage. A careful examination and product analysis for this synthesis is still incomplete, but the product appears to be $B_5H_9 \cdot 4N_2H_4$, analogous to the compound formed with ammonia. It appears to be more stable at room temperature than $B_2H_6 \cdot N_2H_4$.

A few mg. of ethyldecaborane were combined directly with hydrazine. No violent reactions were observable at room temperature, nor was hydrogen evolution very great. In the appropriate stoichiometric explosive mixture of $B_{10}H_{13}Et + 5N_2H_4$, a clear viscous liquid was formed. The liquid gave a possible detonation in the drop hammer test and appears to have promise as a test material. All of the borane-hydrazine compounds are very sensitive to air and moisture.

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SYNTHETIC CHEMISTRY - Cont'd.

C. Reaction of Hexachloromelamine with Chlorinetrifluoride

Work has continued on the reaction of chlorinetrifluoride with hexachloromelamine. A thermocouple was incorporated into the reaction chamber and used to follow the temperature on several runs.

Considerably higher internal temperatures were found to exist than had previously been suspected. This lead to the inclusion of a heat transfer agent in the reactor, which has considerably improved the controllability and reproducibility of the reaction. Two runs were made at -18°C, but the results were not encouraging. It appears that even minor modifications in the experimental conditions can produce quite different results both in terms of total yield and in terms of the nature of the product or products. Efforts are now being directed towards the separation, purification and identification of the material obtained under one arbitrary set of conditions.

Investigation of the reaction of chlorine trifluoride with hexachloromelamine continues. The -78° fraction, after treatment with mercury to remove chlorine trifluoride, has been separated into two components by pot to pot distillation on a vacuum line. The more volatile of these has been identified as cyanuric fluoride by its physical properties, infrared and n.m.r. spectra and hydrolysis to cyanuric acid. The less volatile material appears, at present, to be identical with the material reported by Redstone (Rohm and Haas) and is tentatively assigned the structure proposed by them (N,N,N, trichloro-hexafluoro-s-triazine). Efforts are now being directed towards accumulating enough of this material to complete its identification and to study some of its properties. An alternate procedure for the preparation of hexachloromelamine using commercial calcium hypochlorite has been developed.

Investigation of the reaction of chlorine trifluoride with hexachloromelamine continues. The difficulty in recent weeks in obtaining the higher boiling product mentioned in last month's report is now believed to be due to a badly contaminated tank of chlorine trifluoride, and steps are being taken to purify it before use.

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SYNTHETIC CHEMISTRY - Cont'd.

D. Nitration Studies

Work has also continued on the addition of dinitrogen tetroxide to tetrafluoroethylene. Various methods for conversion of the 2-nitro-tetrafluoroethyl nitrite to difluoronitroacetamide are being investigated.

Work has been resumed on the reaction of perfluorobutadiene with N_2O_4. From one run carried out in ether solution at 0° partition chromatography shows the presence of at least 6 compounds. Chemical evidence indicates that there are three types of compounds present; acids, carbonyl compounds, and a neutral compound containing no carbonyl groups. The neutral compound has been tentatively identified from N.M.R. evidence as 1,4-dinitrohexafluorobutene-2. Attempts to isolate the carbonyl fraction by precipitation as the semicarbazones has been unsuccessful. Attempts to evaluate the acid fraction have also failed.

Nitration studies have been undertaken on p-phenylenediamine diacetate, p-dimethoxybenzene and p-dibromobenzene. The first two yield dinitro-derivatives under relatively mild conditions. The product from p-dimethoxybenzene has been identified as 1,4-dimethoxy-2,5-dinitrobenzene. Attempts at hydrolysis of the product from p-phenylenediamine diacetate for identification have been unsuccessful.

E. Miscellaneous

An investigation of the hydration of trinitroacetonitrile to trinitroacetamide has been undertaken. A sample of trinitro-acetronitrile was prepared in a carbon tetrachloride solution, and a small portion of this was purified by pot to pot distillation on a vacuum line. Its vapor pressure was found to be 8 mm at 23°.

The study of the action of various fluorinating agents on N-chloro-isocyanuric acid has been continued. It appears that the use of HF as a moderator for these reactions will not be feasible since it appears to react with the N-chloroisocyanuric acid.

Further attempts are being made to synthesize trinitro-s-triazine by the reaction of silver nitrite with cyanuric chloride. No product other than silver chloride has as yet been isolated.

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SYNTHETIC CHEMISTRY - Cont'd.

About 160 grams of 1,1,2,2-tetrafluorodinitroethane has been purified from the aezeotropic mixture with carbon tetrachloride which was supplied by the Naval Ordnance Test Station at China Lake. The purified product now contains less than 2% carbon tetrachloride.

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