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AFRPL-TR-67-77

March 1967

Final Report

**COMPILATION AND REVIEW OF DATA
ON THE SENSITIVITY AND STABILITY
OF NF COMPOUNDS: A HANDBOOK (U)**

By: M. E. HILL S. K. BRAUMAN R. A. BELL

AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
EDWARDS AIR FORCE BASE, CALIFORNIA

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By: M. E. HILL S. K. BRAUMAN R. A. BELL

SRI Project 6029

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CHEMICAL SYNTHESIS & DEVELOPMENT DIVISION

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FOREWORD

This final report was prepared by Stanford Research Institute, Menlo Park, California, under Contract AF 04(611)-11547 for the Air Force Rocket Propulsion Laboratory. The report covers the period from May 2, 1966 to January 15, 1967.

The program is the responsibility of the Synthesis Research Department of the Chemical Synthesis and Development Division. Scientists working on the program include M.E. Hill, project supervisor, S.K. Brauman, who assisted in the organization of the project and was responsible for the review on thermal stability and decomposition kinetics, and R.A. Bell, who collected and organized the data from the original reports, with early assistance by E.J. Feinler. Empirical formulas and structures were checked by D.L. Ross, C.L. Coon, D. Tegg, M.W. Lerom, and G.J. McDonald. The authors acknowledge the valuable assistance of S.B. Whitehead who typed the data compilation and, with the assistance of J. Lubeck, typed the text of the introduction and discussion sections of the report.

The Air Force Rocket Propulsion Laboratory contract monitor is Dr. William Leahy, RPCS.

This technical report has been reviewed and is approved.

William H. Ebelke
Colonel, USAF
Chief, Propellant Division

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I INTRODUCTION

Under the sponsorship of the Air Force Rocket Propulsion Laboratory, Stanford Research Institute has undertaken to compile and correlate existing sensitivity data on NF compounds. The results of the survey are summarized in two reports, one a special critical evaluation document, and the second a handbook of test data. This handbook is provided by the present report and is to serve as a reference source for investigators in research and development and is intended to provide a guide in synthesis programs and in the evaluation of NF compounds as propellants.

The large effort in synthesis and evaluation of NF compounds during the past eight years has produced many organic and inorganic compounds containing NF groups as the highly energetic oxidizing portion of the molecule. However, the growth of knowledge concerning the reaction chemistry and physical properties of the NF products has not been accompanied by corresponding knowledge of the sensitivity characteristics of the various NF classes, particularly in relation to their production and handling. The information on sensitivity* obtained during synthesis research programs has been primarily incidental and uncorrelated, gathered by laboratories working independently of each other and each using empirical tests, often modified from their "standard" forms. Other sensitivity testing has been reported by laboratories engaged in development programs; however, such testing related only to the compounds involved in specific formulations. Consequently there is a melange of sensitivity information scattered throughout the technical literature. In addition, unsupported generalized statements are frequently heard to the effect that all NF compounds per se are sensitive, while in actuality only certain classes

*For the purpose of this compilation, sensitivity, as an unmodified noun, is defined as the tendency to react with potential or actual destructiveness to a particular stimulus.

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have unusually dangerous sensitivity characteristics. This confused situation is hindering advancement in using the NF compounds, because investigators do not have a single source of information about their sensitivity aspects.

Concern naturally arises about the sensitivity aspects of NF compounds in general, and many groups in industry and government would like to replace "impressions" with a more quantitative basis for making judgments. One of these groups, the Committee on Sensitivity of New Materials, is charged with making recommendations on overcoming the sensitivity problem, but it does not have a working document relating to specific aspects of NF compound sensitivity and desensitization. It is apparent that a study was needed to assemble and correlate existing data and also to summarize the state of the art as related to the sensitivity of NF compounds. The results of such a study are presented below.

This report is divided into three main parts: (a) handbook organization, which discusses the scope of the compilation and how the test results are organized and presented; (b) a brief review of sensitivity test results, which includes a correlation of general sensitivity with compound structure and a discussion of thermal stability and kinetics and mechanisms of decomposition; and (c) the compilation of test data with indexes and references.

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II HANDBOOK ORGANIZATION

A. Scope of the Survey

The sources used for this compilation were primarily reports by contractors and government agencies. Generally, a page-by-page search of these reports was necessary because sensitivity testing of NF compounds was not consistently indexed under the subject headings in CPIA Abstracts or in the Technical Abstract Bulletins, nor was sensitivity testing included as a heading in most report tables of contents. In many laboratories much of the data was obtained for internal use and was not intended as a part of a study. Nonetheless, these data were abstracted because they helped define the general sensitivity problem when added to other incidental information. The survey eventually included data from reports of 45 laboratories of the 80 initially surveyed, covering primarily the period 1960 through mid-1966. Information was obtained on more than 400 compounds from a review of approximately 1,000 reports.

Data selection was uncritical in the sense that no attempt was made to evaluate the correctness of the result or to determine the efficacy of the test used. In general all data and statements were included that in some way define the sensitivity of NF compounds. Consequently, widely divergent results appear in the tabulations for some compounds, a discrepancy which clearly indicates that sensitivity testing is a real problem in itself. Obviously the bulk of quantitative sensitivity data reported resulted from empirical testing. However, the descriptive statements relating to sensitivity were abstracted, especially those which gave chemical and thermal stability information. Unexpected incidents of decomposition or explosions also were included in the tabulations because they shed light on the reality of handling NF compounds. Limitations in time and the difficulty of reproducing large tables and extensive discussions prevented repeating such material in this compilation, but references are given to the

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reports in which these appear. It was necessary to devise a consistent method of reporting data in terms of the test being used; however, in many instances the sources incompletely stated their results and these are therefore repeated in this compilation in fragmentary form.

Sensitivity test data fell roughly into three categories: (a) results of empirical sensitivity tests, which give the response of the compound to an impetus of varying energy being imparted to it from an outside source; (b) results of thermal stability tests, which try to determine if there is an inherent instability in the structural arrangement of the energetic compound; and (c) results of static sensitivity tests, which are probably a reflection of a type of thermal energy input. The tests in category (a) vary in severity and rate of energy input, the most common low energy method being the familiar impact test which subjects a small sample to a falling weight. A test with pressure inputs several magnitudes higher is the "gap" or shock sensitivity test, in which a sample is shocked to high pressure and temperature by an explosion wave from a donor explosive. Thermal stability tests also vary in method of imparting thermal energy to a test sample. Relatively slow temperature increases are introduced until explosion or rapid decomposition occurs in the sample in such tests as differential thermal analysis, autoignition, or hot bar tests. In the vacuum thermal stability test a sample is held at constant temperature, and rapid temperature increases are imparted to the sample in the Wenograd and compression tests. Although not considered a stability test, the friction sensitivity test is related to thermal stability inasmuch as a compound is heated by a mechanically applied shearing action. The spark or static sensitivity test is related to the tendency of a compound to explode from electrostatic discharge.

B. Summary of Tests and Manner of Data Presentation

A brief explanation of the tests abstracted and the manner of presenting their results in this handbook follow:

1. Impact Tests

The impact test is one of the most common small-scale tests used to evaluate possible handling hazards of energetic compounds. Various

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devices have been built which in essence subject a sample of the test compound to a free-falling weight. Variations among the tests arise primarily in the manner of mounting and holding the sample. In some procedures, a small amount of the compound is placed on a metal plate and a weight is allowed to impact the sample. Other methods used, particularly for liquid compounds, include placing the test material in an enclosed cup and striking this assembly with a falling weight. Variations in procedure for liquid samples usually involve control of the bubble size above the liquid or elimination of a bubble entirely.

Bureau of Mines, Picatinny²⁶⁷ Impact Tests. In making a test with the Bureau of Mines apparatus, the powdered sample is spread uniformly on a metal block and a steel plunger is lowered to rest on the sample. The plunger is then hit by a falling weight from a predetermined height. Several trials are made and the data are reported as the minimum height of fall (in centimeters) required to produce explosions in 50% of the trials. Thus the test data for this machine will read, for example, 20 cm, 2 kg (50% point); this means that the sample will fire 50% of the time when subjected to the impact of a 2 kg weight falling from a minimum height of 20 cm. To improve reproducibility and to alleviate tool damage, some laboratories vary this procedure by placing the sample on a piece of sandpaper of known grit size before it is struck by the weight (Type 12 tools).

In testing with the Picatinny apparatus a steel cup is filled with the explosive material, covered with a metal cover, and surmounted with a vented steel plug. The assembly is then struck by a falling weight. Data from this test are reported in inches of height required for a predetermined size of weight to produce a 50% probability of explosion. The most frequent method of reporting impact sensitivity results for propellant ingredients is in energy terms of the weight-height product, such as kilogram centimeters (kg-cm) or kilogram inches (kg-in). The size of weight involved and the results obtained on a standard explosive may also be reported.

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JANAF Liquid Propellant Test (Test 4).²⁶⁸ This test for liquid propellant ingredients is the standard recommended by the JANAF Panel on Liquid Propellant Test Methods. In this compilation the results obtained using this procedure are identified by the term "Olin" after the commercial source of the test apparatus. A small sample of the liquid of standard volume (in order to reproduce the size of cavity above the liquid in each run) is placed within an elastic ring in a steel cup; a diaphragm is then placed above the sample and ring to form a cavity. A piston with a vent hole is placed on the diaphragm and the assembly is subjected to the impact of a 2 kg free-falling weight. A positive result is indicated by rupture of the diaphragm, accompanied by a loud report and destruction of the parts in the assembly; however, some laboratories use other criteria for interpretation of a go or no-go ignition. The test is repeated at different heights, and a 50% point is determined by the up-and-down method. The sensitivity value is given in height of fall for the specified weight to produce a 50% probability of explosion, or in the weight-height product, kg-cm. Data may also be reported for a standard explosive liquid such as nitroglycerine or n-propyl nitrate. The Bureau of Mines²⁶⁹ has recently studied this test and found that results may vary with the type of mount for the apparatus, with misinterpretation of ignitions as negative or positive, and with erosion of sample cups.

Ball Drop Test.⁷⁹ This test is used on very sensitive materials which would have very low impact values when tested by any of the methods described above. The test consists of dropping an 8.3 gram, $\frac{1}{2}$ inch steel ball bearing on a sample placed on a flat plate. The impact height obtained for five consecutive failures is reported as the impact sensitivity. Since the amount of sample under confinement is very small, the test is considered a very mild one. Consequently many common explosive materials give negative results with this test. Positive results are considered to be indicative of extreme sensitivity. The following data give the relative effects of this impact test on common materials.

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<u>Compound</u>	<u>Failure Height (inches)</u>
Lead styphnate	3
Lead azide	12
BTNEU	>45
Ammonium perchlorate (AP)	>45
BTNEU/AP	>45
Nitroglycerin	Cannot be detonated
PETN	Cannot be detonated
RDX	Cannot be detonated
TNT	Cannot be detonated

Modified DuPont Drop Test.⁷⁹ In its sensitivity testing, DuPont has modified the conventional drop weight testing procedure. The primary differences between the DuPont and BuMines or Picatinny apparatus are in the use of a variable weight assembly as the drop weight, the pin and a commercial bronze cup are used for both liquids and solids and both the 50% point and minimum energy level for positive results are reported in kg-cm.

Schlagen Impact Test.¹⁵¹ This is a pendulum type impact test in which the sample is placed in a plastic or aluminum tube container and is struck by weights on a pendulum arm. The amount of energy delivered is varied by changing weights at the end of the pendulum and by changing the starting height of the pendulum. Results are reported in kg-cm, sometimes with a description of variations in sample treatment.

ICI Impact Test.¹²⁷ The apparatus used here consists of a $\frac{1}{2}$ kg mild steel hammer (weight) which is allowed to fall from a predetermined height onto a fixed volume of sample placed between the faces of two steel roller bearings, $\frac{1}{4}$ inch in diameter by $\frac{1}{4}$ inch long. The bearings are suitably held in place by collars and the whole assembly rests on a steel plate. The maximum height for detonation failure for ten attempts and height for at least one positive result are reported. Values obtained for standard explosives are:

RDX	25-30 cm
PETN	30-40 cm
Tetryl	60-70 cm
NG	25-30 cm
TNT	Negative

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2. Shock Sensitivity Tests

Good correlation has been obtained in the explosives field between shock sensitivity tests and field handling experience. The shock test is used in the propellant field to order sensitivity of propellant ingredients and formulations relative to known compounds.

Gap Test.^{268,270} This test is used for direct evaluation of shock-induced detonability of materials. It consists of transmitting a high energy shock wave from a donor through a "gap" filled by an attenuating material of plastic to the acceptor, which is the test sample. The distance between the donor and acceptor is varied and the results are reported in terms of 50% probability of explosion. The more sensitive propellants give a large gap test value (reported in terms of "cards" or inches) because they can be initiated by a weak shock (caused by attenuation through a larger gap of plastic); the least sensitive materials have a small value. Data for known explosives may also be reported for comparison. Caution should be used in interpreting the meaning of gap test values since the results of this test are known to be influenced by the geometry of confinement and kind of container materials.^{254,256}

Base Load Test.⁷⁹ This test was used by DuPont to measure the susceptibility of solids and liquids to explosion when initiated by a standard explosive charge. The "base load" is the material to be tested and is contained in a commercial cap shell. The base load charge is fixed at a constant volume. The initiating charge is a DuPont E-94 cap placed in contact with the test material. The assembly is placed on a lead witness plate and the cap is initiated. Relative energy release is determined by comparing the size of the indentation or hole in the lead plate with a standard series using NF, PETN, and lead azide. The standards are numbered from 0 to 6, with 0 being the most positive designation for a strong detonation.

3. Thermal Stability Tests

Long-term storage stability and stability to the conditions encountered in developing, manufacturing, and using an ingredient in a

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rocket motor are of great importance. Information about the stability of a particular material is obtained early in the research phase by any of several small-scale accelerated test methods. Each test gives results which are informative when related to a standard compound whose thermal stability is well known, and some correlate well with long term storability.

Vacuum Thermal Stability.²⁶⁷ The vacuum thermal stability test simply measures the amount of gas given off from the sample at a predetermined constant temperature under reduced pressure. Several variations of the following basic method have been reported, primarily in the manner of heating the test sample and assembly of apparatus. A weighed sample is placed in a glass heating tube of known volume which is suitably connected to a calibrated glass capillary tube and to a vacuum pumping system. The capillary tube is terminated by a mercury reservoir. The system is evacuated to a pressure of about 5 mm of mercury and the level of the mercury which rises in the capillary is marked and recorded. The heating tube is maintained at the desired constant temperature, usually 60, 90, or 100°C, until the sample decomposes or for a predetermined period of time. The volume of gas liberated is calculated from the difference in initial and final stages of the mercury, the volume of the capillary tube per unit length, and the volume of the heating tube reduced to standard temperature and pressure. Results are reported in cc of gas per gram of test sample for the length of the test in hours at the temperature used: cc/g/hrs/°C. Explosives in use today are quite stable and evolve very little gas by this test. Compounds which give more than 3 cc/g/48 hrs/100°C are considered relatively unstable and may not be usable as ingredients. Impurities in very small amounts can drastically affect the results; consequently, high purity of the test sample is an absolute necessity.

Variations of this test may be found in references 99, 127, and 271.

Taliani.^{273,274} The Taliani thermal stability test differentiates between stable and unstable compounds by the increase in pressure with time in a constant-temperature, constant-volume system containing the test sample and air, nitrogen, or other gas. The apparatus is similar

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to the vacuum thermal stability apparatus except that the volume is maintained constant by a mercury leveling device. Data are obtained in terms of pressure change, converted to STP conditions, and reported as cc of gas evolved per gram of sample at the chosen temperature and time interval.

Wenograd.^{155,275,276} The Wenograd thermal sensitivity method measures the time delay to explosion as a function of temperature. The sample is loaded into stainless steel hypodermic needle tubing and is rapidly heated by a capacitor discharge to temperatures giving explosion time delays from about 50 μ sec to several milliseconds. Data may be reported as a plot of the $\log_{10}$ time delay in milliseconds versus reciprocal temperature and compared in the same plot with results from a standard explosive. Alternatively, the temperature for thermal initiation at 250 μ sec may be reported for the test compound. When compounds are compared, the one requiring the highest temperature for thermal initiation is considered to be the least sensitive, and the compound requiring the lowest temperature for initiation is considered the most sensitive. A correlation of test results with impact sensitivity and supporting evidence has been reported.²⁷⁵ The Wenograd test has been studied by Roth,²⁷⁷ who suggested that explosion delay times are induction times for chemical reactions involving a vapor phase; he also found that some correlation with other tests may be possible.

Differential Thermal Analyses.¹⁹⁷ This method essentially involves the thermal decomposition analysis of a test material in comparison with an inert reference material being heated at the same time. The apparatus consists of a temperature programming and control system, a furnace with control thermocouple and with the readout reference and differential thermocouples inserted at the geometrical center, and an amplifying and recording system for the readout thermocouples. The output, ΔT , of the differential thermocouple in the test specimen forms the y axis of an x-y recorder and the output of the thermocouple in the reference material versus 0°C, in the x axis. Thus a sample is heated at a constant rate until it decomposes, as evidence by an exotherm being recorded as a change in slope in ΔT above the base line, often as a very sharp peak.

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The decomposition temperature is reported as the temperature on the x axis at which the exotherm occurred. When solid samples melt or liquid samples boil the change in phase is recorded as an endotherm, or a change in ΔT below the base line.

Thermogravimetric Analysis.²⁷⁸ Thermal analysis of a sample on a thermobalance is used to detect and record the change in mass of the substance being heated as a function of temperature or of time, or to record changes as a function of time in a sample held at constant temperature. Data are recorded as an x-y plot and the results of the analysis may be reported as percentage loss in a period of time at a specified temperature or percentage loss over a temperature range.³⁸

Copper Block Test.⁷⁹ This is an autoignition test designed by DuPont. A cylindrical copper block with vertical holes to contain the material and a thermometer is used to obtain the autoignition temperature of materials. Material to be tested is placed in a test tube and inserted into the block. The top of the tube is covered and the whole assembly is placed on a hot plate adjusted to give a temperature rise of about 5°C per minute. The temperature at which fume-off or explosion occurs is recorded. This test gives more confinement and more control of heat-up than does the hot bar, and in general gives more reproducible results.

Hot Bar Test (DuPont).⁷⁹ A Parr-Dennis melting point apparatus is used to determine the unconfined decomposition temperature of energetic materials. Tests are run to obtain the time to decomposition or explosion at 250°C.

This test is a fast measure of short-time explosion or decomposition temperature and requires very small amounts of material. However, the results are influenced by the amount of material used, physical condition of material, condition of hot bar surface, and lack of confinement.

The apparatus consists of a copper bar 17 inches long and 1 inch square, silver plated, and heated at one end to provide a temperature gradient along its length. The surface temperature of the bar is measured with a copper-constantan thermocouple mounted on a sliding arm

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and connected to a potentiometer which reads directly in °C. Bar temperatures may be adjusted to 300°C.

Autoignition (Esso).^{115, 116} An explosion temperature test has been modified by Esso for comparison of the thermal sensitivity of very high energy compounds. A sample is contained in the freshly polished empty copper cup of a No. 8 blasting cap whose bottom has been accurately ground to a thickness of 0.08 mm. The cap is then sealed by a Teflon plug, leaving an air space above the sample. The sample is clipped to a plunger and lowered into a molten Woods metal bath held at a known temperature. The delay between the time the sample enters the bath and explosion of the sample is noted. This explosion delay time is measured versus temperature for several temperatures preselected to give a range of delay times from 0.1 to about 10 seconds. The data have been used to calculate kinetic parameters.

Friction Sensitivity.

1. Esso.¹¹⁴ Esso has designed a friction test device for very sensitive materials which pinches the sample between steel plates in the presence of grit in order to avoid the gross heating and impact forces of the pendulum friction sensitivity tester. A 1-inch-diameter stainless steel machine screw with polished end bears on a flat polished surface with the sample and added grit between the screw end and plate. Thus the test material is subjected to slow shear in the presence of grit under monotonically increasing pressure as the screw is turned. The dominant test variable is the Mohs hardness of the added grit, with harder grit making the test more severe. Data from the test are reported in Mohs hardness of the grit needed to produce a positive test. Nitroglycerin gives a negative test for bare tools and grit hardness numbers of 5.5 and 10. Other negative tests are given by tetryl and PETN, and lead azide gives a positive test at 5.5 Moh hardness. Therefore materials with positive tests with grit at any hardness or with bare tools are more sensitive than these standard explosives.

2. Aerojet.²⁷² Aerojet uses a rotational friction tester which moves the sample against a stationary ram holding loads of various sizes. The sample is placed in a circular groove in the rotating portion

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of the device and a mating stationary ram is placed on the sample. The sample holder is rotated at speeds from 400 rpm up to 7000 rpm. Loads on the stationary ram can be increased to 4000 g. Tests have shown that very sensitive materials generally decompose, ignite, or explode within a few seconds, before the sample holder has reached autoignition temperature. Data are reported in rpm and load size to obtain a positive test. Thus the sensitive materials give a positive test at low load and rpm. A relative friction sensitivity factor is also used, obtained by multiplying load by rpm by 10^{-6} , e.g., a sensitive material with positive test at 500 rpm and 500 g has a relative number of 0.25.

4. Spark Sensitivity Tests

Many accidents in the explosive and propellant fields have been attributed to electrostatic discharge. Consequently several tests have been devised which pass a spark of known energy through the test sample. The energy required for explosion is related to the amount of static potential it is possible for man to accumulate.

Spark (Static) Sensitivity.⁷⁹ A test used by DuPont is designated the "leg to shell" test. The test material is confined in a cylindrical cap shell and static discharge takes place through the sample between buried bridge posts. The usual method of reporting results is by comparison with the electrostatic charge which might be built up on a human body under ideal conditions. Capacitance measurements on an individual have ranged from 0.0001 to 0.0004 μfd . A reasonable value seems to be 0.0003 μfd . The maximum static potential that a man can accumulate is about 10,000 volts, equivalent to 0.015 joule. A material which can be ignited by static electricity with energies near or below 0.015 joule or 10,000 man-equivalent volts (M.E.V.) is considered too hazardous for handling unless the possibility of static discharge can be eliminated.

Esso²⁷⁹ uses a test similar to the Bureau of Mines spark tester.²⁸⁰ In this apparatus capacitors in the range of 500-8500 picofarads are charged to 5 to 15 kilovolts and discharged from a needle point through the sample. Data are reported in joules and compared to the static

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potential of a man. Other spark testers operate on the same general principle of point source to ground for the discharge and through the test sample. Platt and Ford²⁸¹ have described a similar wire-to-ground electrostatic test device for hydrazine diperchlorate and have included descriptions of other empirical tests used by Thiokol on propellant materials.

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III DISCUSSION

A. Structure Sensitivity Relationships

1. Introduction

In this section we discuss some correlations between the sensitivity of NF compounds and their structures. When considering the large number of individual pieces of data summarized in Section IV, it is natural to be concerned with general conclusions that can be drawn and with the overall present state of the art in the NF sensitivity field. It would be desirable to rank NF compounds of various structures by some quantitative test number or weight factor derived from a set of numbers. Unfortunately for an evaluation or comparison on a quantitative basis, the reported results are too inconsistent and confusing. However, if we evaluate the information in the search for general trends and correlations, some useful information can be distilled from the mass of data. Therefore, we shall attempt to point out in this section some valid relationships between the sensitivity characteristics of NF compounds and their structures.

Propellant ingredientsensitivity has followed the same general trend as explosive sensitivity--namely, sensitivity becomes more severe with an increase in the compound's energy, which can be stated in various ways such as fluorine balance, NF_2 to carbon ratio, or heat of explosion. Much of the desensitization work on propellant compounds has shown results similar to those for explosives; for example, dilution of the very energetic NF materials is the most effective way to desensitize them. Explosives technology relating to manufacture and handling is applicable to NF propellant ingredients; however manufacture and handling of NF compounds involve sensitive liquids more frequently.

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Attempts to prepare correlation tables revealed that results of tests in various laboratories are not directly comparable and are inconsistent even on the same compounds. There are several reasons for this situation. Results of many tests are greatly influenced by physical factors, such as variations in design of test equipment, small deviations in test procedures, humidity, or materials of construction. Variable interpretation of test results by different laboratories introduces another factor of error in the quantitative measure. And results in NF compound sensitivity measurements are particularly influenced by impurities. (We often found little evidence of purity control.) This immediately creates some doubt regarding the validity of the result as a quantitative measure of the test compound's sensitivity to that particular test.

Many laboratories have modified standard tests for internal use, or they have devised new tests in an effort to simulate an actual handling situation. All of these changes make it difficult to evaluate the real situation. However, several laboratories have used a variety of tests on a large number of compounds within a general class. Since such results were obtained in the same laboratory on the same devices, as for example the Esso tests on a series of tris-difluoroamino methoxy compounds,²⁸⁴ they are useful for detecting structural effects.

The following discussion is a qualitative review of the sensitivity situation for NF compounds falling in the classes of alkanes, ethers, esters, guanidines, and compounds of high nitrogen content, with additional comment on mixed group compounds such as $\text{NO}_2\text{-NF}_2$. Thermal stability is discussed only as it pertains to sensitivity situations. This discussion includes consideration of compounds which are more sensitive than nitroglycerin or cyclotrimethylenetrinitramine (RDX) according to specific tests.

2. Alkanes

Sensitivity tests and related work on members of the difluoroamino alkanes have provided an excellent basis to determine substituent effects by the NF_2 group on a carbon chain. This has been particularly true of

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bis-difluoroamino alkanes, since research on all of the isomers of the bis-NF₂ propanes and some of the butanes has been relatively extensive. Consequently structure-sensitivity relationships can be determined relative to NF₂ position in the compound or carbon branching without being influenced by some other functional substituent. A few of the isomeric structures of the tris-difluoroamino alkanes have been prepared and the available sensitivity information permits some comparisons with tris-difluoroamino methyl compounds. Some of the data used is summarized in Table I.

Mono-difluoroamino compounds are relatively few in number and relatively little sensitivity test data are available. The simplest member, H₃CNF₂, is known to be quite sensitive and has been involved in explosions in vacuum lines and in preparation.²⁸² Tertiary-butyldifluoroamine (221a)* is not sensitive to impact and is thermally stable to 125°C; its decomposition mechanism is discussed below. Tritryl difluoroamine (390) is stable at 90°C.

In the bis-difluoroamino alkane series correlations can be made relating to the ratio of NF₂ to carbon and position of NF₂ on the carbon chain. As one may expect, bis(difluoroamino)methane (43) is quite sensitive to impact and thermally unstable. Of the two-carbon bis isomers reported, 1,2-bis(difluoroamino)ethane (80) is sensitive to impact and is much more sensitive than nitroglycerin. 1,1-Bis(difluoroamino)ethane (79) is thermally unstable and, by analogy to other compounds on the basis of NF₂ to carbon ratio, is probably quite sensitive.

Distinct positional effects of the NF₂ group on the carbon chain are quite discernible in the propane series. All of the four propane isomers have been studied in a fundamental research program in which differences in thermal and chemical stability and in detonation characteristics are significant to practical situations in manufacture and handling.²¹¹⁻²²⁴ Empirical testing information qualitatively indicates

* In this section a number in line within parentheses is the number assigned to the compound in Section IV "Compilation of Raw Data." If no number is given, the compound is referred to by acronym. The compound number can be obtained from Appendix A which lists acronyms for the compounds and the corresponding numbers.

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Table I
SENSITIVITY DATA OF SOME DIFLUOROAMINO ALKANES

Compound No.	Structure	Impact Sens. 50%	Static	Thermal Stability	Other
221a	$(H_3C)_3CNF_2$	~ 39 kg in; RDX=10 kg in		Stable to 125°	
390	$(C_6H_5)_3CNF_2$			DTA: Exo, 138° VTS: 2.3cc/g/100h/90°	
43	$CH_2(NF_2)_2$	0.1 kg cm		Unstable at 25°	
80	$F_2NCH_2CH_2NF_2$	11 kg in; RDX=20 kg in	~ 8200 M.E.V.		
79	$CH_3C(NF_2)_2H$			VTS: 26cc/g/100h/90°	
128	$CH_3C(NF_2)_2CH_3$		Very sens.	Wenograd: 250μsec delay, 507°	Card gap=187 cm for Low Velocity Detonation
126	$CH_3CH(NF_2)CH_2NF_2$	2.8 kg in; RDX=10 kg in	25,600 M.E.V.	VTS: 0.1cc/g/100h 90° Wenograd: 250μsec delay, 551°	Card gap ~ 95 cm for Low Velocity Detonation
127	$F_2NCH_2CH_2CH_2NF_2$	>170cm/2 kg	Very sens.		
125	$CH_3CH_2CH(NF_2)_2$			VTS: 0.4cc/g/100h/60°	
213	$F_2NCH_2C(CH_3)(NF_2)CH_3$	5.7 kg cm			
210	$[CH_3CH(NF_2)-]_2$	32 kg in		DTA: Exo, 264° VTS: 1.3cc/g/100h/90°	
208	$CH_3CH_2CH_2CH(NF_2)_2$	2.5 kg cm			
209	$CH_3C(NF_2)_2CH_2CH_3$	4.0 kg in			

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Compound No.	Structure	Impact Sens. 50%	Static	Thermal Stability	Other
74	$F_2NCH_2CH(NF_2)_2$	1-5 kg in			
122a	$F_2NCH_2CH_2CH(NF_2)_2$				
122b	$CH_3C(NF_2)_2CH_2NF_2$				
123	$F_2NCH_2CH(NF_2)-CH_2NF_2$	7-18 kg cm		Stable at 60° VTS: 0.9cc/g/100h/90°	Exploded on handling.
31	$C(NF_2)_4$	42 kg cm		DTA: Exo, 250°	
247	$[F_2NCH_2CH(NF_2)-]_2-CH_2$	16 kg cm	10,950 M.E.V.	DTA: Exo, 228° VTS: 0.4cc/g/100h/90°	
286	$\frac{CH_2CH_2C(NF_2)_2CH_2-}{CH_2C(NF_2)_2}$	5 kg cm			Shock sens.
309	$CH_3C(NF_2)_2CH_2CH_2-CH(NF_2)CH_2NF_2$				
310	$[F_2NCH_2CH(NF_2)-CH_2-]_2$	1 kg cm		DTA: Exo, 205°	
353	$(F_2N)_2CH-\text{C}_6\text{H}_4-CH(NF_2)_2$	2.8 kg in			
293	$[F_2NCH_2CH(NF_2)-CH(NF_2)-]_2$	106 cm/2 kg		VTS: 2.6cc/g/100h/90°	

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that the geminate compound 2,2-bis(difluoroamino)propane (128) is much more sensitive than the 1,2-isomer (126) to impact, and that it is in the nitroglycerin range. The 1,2-propane did not show unusual sensitivity in its tests. The 1,3-isomer (127), having the two NF_2 groups separated by a CH_2 group, appears to be much less sensitive to the impact test than the other isomers. However, the 1,1-, 2,2-, and 1,3-bis(difluoroamino)propanes exhibit a high degree of sensitivity to static discharge. The 1,3-isomer is relatively the least sensitive, the 2,2-compound next, and the terminal geminate, 1,1-DP, is the most sensitive. Comparative static sensitivity for the 1,1-isomer versus the 2,2-isomer was obtained when the compounds were prepared for shipment.²⁸³ For shipping purposes, a 3-to-1 dilution of 2,2-DP (128) by Arochlor was necessary to eliminate initiation to detonation, whereas explosion by spark in the 1,1-DP (125) could not be eliminated unless it was diluted fivefold.²⁸³ The static sensitivity of 1,2-DP (128) seems to be somewhat less than that of the other propane isomers.⁷⁹

A study of the explosion phenomena of the bis propane isomers by an SRI laboratory has revealed some rather significant information concerning their initiation and propagation of explosion.^{211-224, 258} The compounds exhibit both a low velocity (LVD) and a high velocity detonation wave (HVD), and have a very small critical diameter for transition from HVD to LVD when initiated in heavy lead confinement. For 1,1- and 2,2-DP (125, 128) the transition diameter for the high to low velocity is about 4.0 mm, and for the 1,3- and 1,2-isomers it is about 1.6 mm. The failure diameters for the low velocity wave in all the isomers are below 1.5 mm. These measurements indicate that there is no practical diameter below which these NF compounds will not propagate at either low or high velocity. A study of the low velocity detonation (LVD) phenomenon in the gap test configuration showed that 1,2- and 2,2-DP were easy to initiate at low shock pressures and that LVD wave is easily obtained. Low velocity detonation was initiated by shock waves which had been attenuated by 187 cm (about 5.5 ft) of Plexiglas in 2,2-DP and about 95 cm for 1,2-DP.²⁵⁸ The LVD waves are damaging; consequently, if the phenomenon

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is characteristic of a broader range of NF compounds, a serious problem exists in the manufacture and handling hazard of NF liquids. The bis propane isomers show good thermal stability as a group. Various studies of their decomposition kinetics and mechanisms are reviewed below.

Relatively little information is available on the butane bis-NF₂ isomers. One of these, IBA (213), has had some study in empirical tests which show possibly a little less sensitivity than for the corresponding 1,2-propane isomer. The critical transition diameter for high to low velocity detonation is higher than the propanes--10 mm as against 4 or 1.6 mm--but this is not of practical significance. The IBA and its isomer, 2,3-DB (210), both have the ease of initiation characteristic that the propanes do. Reported impact sensitivities of the 1,1- and 2,2-bis-(difluoroamino)butanes (208, 209) indicate that they were highly sensitive even if the test results were two orders of magnitude too low. A limited amount of spark and impact test data in uncontrolled experiments suggests that the geminate group may impart sensitivity to a compound regardless of the size of the molecule. Some support for this generalization is indicated by the results obtained at NOI in the Wenograd test of the thermal sensitivity of a series of geminate and vicinal alkanes containing up to six carbons.¹⁵⁵ There was relatively little change in temperature at 250 μ sec delay of explosion for the 2,2-geminate compounds, whereas the 1,2-vicinal compounds had the expected increase in temperature at 250 μ sec delay (i.e., they were less thermally sensitive as the molecular dilution by CH₂ groups increased). The 1,1 or terminal geminate series did not follow this relationship; 1,1-DP was more sensitive than 2,2-DP and 1,1-bis(difluoroamino)hexane was less sensitive than the 2,2-hexane isomer.²⁴⁴ The general indication, however, appears to be that the geminate group sensitizes a structure toward initiation.

Tris-difluoroamino alkanes generally follow the sensitivity characteristics expected of compounds having about a one-to-one or greater ratio of NF₂ to carbon. Also, the effect of geminate groups appears to hold in the tris examples reported. 1,1,2-Tris(difluoroamino)ethane (74) is extremely sensitive and somewhat unstable. Similar extreme

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sensitivity was shown by 1,1,3-tris(difluoroamino)propane (122a), which exploded as a cap was removed from its container.²⁸² Thus the overall evidence of having a geminate group on the terminal carbon indicates that 1,1-bis compounds may be particularly susceptible to low energy impetus on the basis of the few observations recorded. A comparison with the tris isomer, 1,2,2-bis(difluoroamino)propane (122b), cannot be made because of the lack of comparable test results; however, this compound has been successfully handled and shipped to this laboratory in solution.²⁸² The vicinal tris-compound having NF_2 at the 1,2,3 positions, 1,2,3-tris-(difluoroamino)propane (123), is still so sensitive that no correlation can be made with the 1,1,2-or 1,2,2-compounds to determine if there is a positional effect. The thermal stability of the 1,2,3-tris compound seemed reasonable at 90° for 100 hours.

The ultimate in NF_2 substitution on carbon, Compound Delta, $\text{C}(\text{NF}_2)_4$ (31), has been the subject of several sensitivity tests. Its sensitivity to impact did not seem unusually low. However it was more shock sensitive than lead azide, and in other tests it appeared to be comparable in sensitivity with Compound R and PFG (30, 26). (Compound R and other tris methyl compounds are discussed in context with the tris methoxy compounds.) Decomposition of Delta is discussed in Section III-6. Other tetrakis NF_2 compounds were quite sensitive; the 1,2,4,5-tetrakis pentane (TDP) (247) detonated in the DuPont ball drop test, showing a sensitivity greater than nitroglycerin. Sensitivity of TDP was also shown by a positive result in the static sensitivity test at an energy level equivalent to the charge accumulatable on a human being. Extreme sensitivity (greater than NG) was characteristic of the six carbon tetrakis compounds, either cyclic or straight-chain (286, 309), and regardless of the separation by methylene groups of vicinal NF_2 groups (310). The 1,1-geminate effect shows up in a more diluted tetrakis compound: the compound, $\alpha, \alpha, \alpha', \alpha'$ -tetrakis(difluoroamino)xylene (353), having a ratio of NF_2 to carbon of one to two, was very impact sensitive. Compounds with more than four NF_2 groups follow the same trend as the other alkanes. However, an unusually high impact sensitivity value was reported for 1,2,3,4,5,6-hexakis(difluoroamino)hexane (293). Thus it is out of

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line with the other compounds and difficult to rationalize if further testing should confirm the early test values.

From the general data that have been published some generalizations can be made about the relative sensitivity of the vicinal and geminate NF_2 groups. The geminate groups impart more sensitivity to a compound than do vicinal, particularly when the geminate group is terminal, i.e., in the 1,1-position. The geminate compounds are quite sensitive generally and appear especially susceptible to spark and shock initiation. Evidence also indicates that the geminate group cannot be desensitized by lengthening the carbon chain. Separation of two NF_2 groups by a CH_2 group appears to make the compounds less sensitive, although not enough data are available to confirm this.

3. Alcohols

As a class the alcohols are not represented by a large number of compounds. The primary alcohol, 2,3-bis(difluoroamino)propanol (130), does not appear to be unusually sensitive; its test results, where they could be compared, were about the same as for 1,2-DP. Consequently no particular benefit can be ascribed to the hydroxyl group on the basis of the reported test values. However, the 2,2-geminate isomer (129) was much more sensitive on the basis of the impact value; this seems within the trend of the effect of substitution in the alkane series. The consistency of the geminate trend is also supported by the sensitivity of 2,2-bis-(difluoroamino)propanediol (131), which is reported to be very sensitive to friction and to have a low impact sensitivity value. The vicinally substituted tetrakis(difluoroamino)hexane-3,4-diol (311) is not unusually sensitive, compared to the other alcohols (Table II).

4. Esters

Esterification of the bis-difluoroamino alcohols appears to have some desensitization effect (Table II). The formate ester of 2,3-bis(difluoroamino)-propanol (188) has impact and static sensitivity values in the same range as the parent alcohol, but the acetate ester (241) is

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Table II
SENSITIVITY DATA OF SOME NF₂ SUBSTITUTED ALCOHOLS, ESTERS, AND ETHERS

Compound No.	Structure	Impact Sens. 50%	Static	Thermal Stability	Other	
<u>Alcohols</u>						
129	$\text{CH}_3\text{C}(\text{NF}_2)_2\text{CH}_2\text{OH}$	5.6 kg in	Rel. insens >77,500 M.E.V. >77,500 M.E.V.	DTA: Exo, 161° VTIS: 60cc/gm/100h/60°	Card gap: 1.21 in; NG=0.91 in	
131	$\text{HOCH}_2\text{C}(\text{NF}_2)_2\text{CH}_2\text{OH}$	16.5 cm/2 kg				
130	$\text{F}_2\text{NCH}_2\text{CH}(\text{NF}_2)\text{CH}_2\text{OH}$	12.3 kg cm				
311	$[\text{F}_2\text{NCH}_2\text{CH}(\text{NF}_2)\text{CH}-(\text{OH})-\text{J}_2$	>56 in/2 kg				
<u>Esters</u>						
106	$\text{F}_2\text{NCH}_2\text{CH}(\text{NF}_2)\text{OOCH}$	90 kg cm	38,400 M.E.V.	DTA: Exo, 225°		
188	$\text{HCOOCH}_2\text{CH}(\text{NF}_2)-\text{CH}_2\text{NF}_2$	35 kg in; RDX=15.5 13 in/5 kg; NG=6 in/5 kg	>77,500 M.E.V.			
242	$\text{CH}_3\text{C}(\text{NF}_2)_2\text{COOC}_2\text{H}_5$	2.8 kg in	>77,500 M.E.V.			
241	$\text{F}_2\text{NCH}_2\text{CH}(\text{NF}_2)-\text{CH}_2\text{OCCCH}_3$	>480 kg cm	>77,500 M.E.V.			
281	$\text{CH}_2=\text{CHCOOCH}_2\text{CH}-(\text{NF}_2)\text{CH}_2\text{NF}_2$	>100 cm/2 kg 96 kg cm 5 kg cm; n-PN=8 cm	>77,500 M.E.V.			
287	$\text{F}_2\text{NCH}_2\text{CH}(\text{NF}_2)-\text{CH}(\text{NF}_2)\text{CH}(\text{NF}_2)-\text{OOCCH}_3$	60 kg cm	13,700 M.E.V.			

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Table II
SENSITIVITY DATA OF SOME NF₂ SUBSTITUTED ALCOHOLS, ESTERS, AND ETHERS

Compound No.	Structure	Impact Sens. 50%	Static	Thermal Stability	Other
346	$F_2NCH_2CH(NF_2)CH_2-COOCH(NF_2)CH(NF_2)-CH_3$	390 kg cm		DTA: Exo, 250°	
347	$F_3NCH_2CH(NF_2)CH_2-$	135 kg cm	>77,500 M.F.V.		
<u>Ethers</u>					
187	$F_2NCHCH(NF_2)CH_2OCH_2$				Stability: poor
159		5 kg in			
199	$[F_2NCH_2CH(NF_2)-]_2O$	2 to 3 kg cm	28,300 M.F.V.		Wenograd: Temp, μsec, 565°
162	$CH(NF_2)CH(NF_2)CH-(NF_2)CH(NF_2)-$	2.3 kg cm	18,250 M.F.V.	DTA: Exo, 193° VTS: 1 cc/g/100h at 90°	
294	$[F_2NCH_2CH(NF_2)CH(NF_2)-]_2O$	2.3 kg cm; NG=10 kg cm	>0.43 joules	DTA: Exo, 232° VTS: 1.0 cc/g/100h at 90°	
377	$[F_2NCH_2CH(NF_2)-OCH_2-]_2CHOCH(NF_2)-CH_2NF_2$	2.3 cm/2 kg 6.0 kg cm; NG=10 kg cm	pos., 2 joules	DTA: Exo, 265° VTS: <1cc/g/100h at 90°	Card gap: 1.05 in; NG=0.9 in
361	$[F_2NCH_2C(NF_2)_2CH_2-OCH(NF_2)-]_2$	2.5 kg in	0.13 joules	DTA: Exo, 185°	Card gap: 1.03 in; NG=0.9 in

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much less sensitive. Both the formate and acetate esters of 1,2-bis (difluoroamino)-ethanol (106, 187) are less sensitive than the corresponding 1,2 ethane, according to the impact, ball drop, and static sensitivity tests. A similar trend toward desensitization is shown by the acetate ester of 1,2,3,4-tetrakis(difluoroamino)-1-butanol (287). Other reported saturated esters have a large carbon to NF_2 ratio and are not particularly sensitive. Two isomeric examples having the NF_2 group in both the acid and alcohol portions were found to differ only in impact sensitivity (346, 347). The ethyl ester of 2,2-bis (difluoroamino)propionic acid (geminate NF_2 group) was sensitive to impact, maintaining the general characteristic of geminate bis NF_2 compounds.

Data on unsaturated esters indicate that the presence of the olefinic group in either the alcohol or acid portion has no discernible effect, certainly not in the direction of sensitization. However, none of the reported esters has a high NF_2 to carbon ratio, and as a class these compounds are not particularly sensitive. The acrylate ester of 2,3-bis(difluoroamino)propanol, NFPA (281), a much used monomer, tests as an insensitive, handleable compound according to all of the reported data.

A series of Wenograd thermal sensitivity tests was run on a variety of carbamates.¹⁵⁵ All were less thermally sensitive than nitroglycerin and most were less thermally sensitive than bis(fluorodinitroethyl) formal, FEFO, or the corresponding NF_2 alkanes or alcohols. Again, compounds having the higher NF_2 to carbon ratios were relatively more sensitive. No effect by the NH group of the carbamates was discernible, the compounds being more like the corresponding esters.

5. Ethers Containing Mono- or Di-Substituted Carbons

The NF_2 ethers, Table II, have the sensitivity characteristics of the corresponding hydrocarbon radical, and when highly substituted with NF_2 groups are very sensitive. Thus $\alpha, \alpha', \beta, \beta'$ -tetrakis(difluoroamino)ethyl ether, TDEE (199), and hexakis(difluoroamino)propyl ether, HPE (294),

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are more sensitive than nitroglycerin by an order of magnitude. Desensitization of HPE was best obtained by dilution. A similar highly sensitive cyclic ether is the 2,3,4,5-tetrakis(difluoroamino)tetrahydrofuran, THFA (162). The corresponding 2,5-bis(NF₂)-2,5-dihydrofuran(159) was somewhat less sensitive, as would be expected from the larger carbon to NF₂ ratio. Considerable handling experience has been obtained on TVOPA (377), an adduct of N₂F₄ and this vinox propane, which is highly substituted with NF₂ and has given test results indicating greater sensitivity than nitroglycerin. Careful quality control of the preparation of this compound has obviated many of its handling difficulties. OPE (361), an ether of high NF₂ to carbon ratio, is an example of a 1,2,2-tris-difluoroamino-substituted compound that is very sensitive (>NG). Other variations in structures in compounds such as the epoxides, acetals, and cyclic ethers apparently have no sensitivity advantages. The ethers did not appear to be unusually unstable thermally; however, it was difficult to obtain pure compounds for testing.

6. Tris(difluoroamino)methyl Compounds

A large number of compounds have been synthesized that contain the tris(difluoroamino)methoxy group, (NF₂)₃CO-. Without exception the tris-methoxy derivatives have been extremely sensitive by any test method, have left much to be desired in thermal stability, and seem particularly susceptible to initiation by low input of energy. The tris(difluoroamino)-methoxy group seems to determine the sensitivity characteristics, since low energy compounds which contained no energetic group other than the tris-NF₂ methoxy group were always quite sensitive. The tris-methoxy compounds containing nitro or nitrate groups seem not to be more sensitive as a class, nor was a practical beneficial effect discernible. However, it does appear that the nitro-containing tris-methoxy compounds are not as static-sensitive. Salts of tris methoxy substituted amines and perchloric acid, such as INFO 635 (137), are ultrasensitive and particularly susceptible to initiation by low energy input.

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A study of the sensitivity and desensitization of tris(difluoroamino)-methoxy compounds has recently been completed by Esso.²⁸⁴ These workers concluded that the ultrasensitivity of the $-\text{OC}(\text{NF}_2)_3$ derivatives could not be overcome sufficiently to be equivalent to handleable conventional explosives, on the basis of a survey of 45 compounds tested in their own laboratory on the same test equipment. The compounds included examples of $-\text{OC}(\text{NF}_2)_3$ substituted alkanes, ethers, alcohols, nitro compounds, and nitrate esters, with little distinction in sensitivity characteristics; in general, they are more sensitive the higher their heats of explosion. Desensitization methods which appeared to succeed according to one test did not show a desensitization effect when another test was used. As for other classes, dilution was the most effective method of desensitization but with a loss in energy. The Esso workers felt that propellants can be obtained in the 285-290 I_{sp} range, with sensitivity characteristics similar to double base propellants, by desensitizing by dilution or inhibition, provided hard particles are avoided in the formulation. Some are summarized in Table III.

Analogous to the tris(difluoroamino)methoxy derivatives, compounds of the general type $(\text{NF}_2)_3\text{CN}-$ or $(\text{NF}_2)_3\text{C}-$, as exemplified by BTU (96) and BT-Biuret (153), have all been extremely sensitive--more so than PETN or nitroglycerin--and are borderline in thermal stability. Various attempts to desensitize some of these compounds have been unsuccessful.

7. Nitro- NF_2 Compounds

Compounds containing nitro groups have been synthesized for the effect of the nitro group on the derivatives' properties, such as increasing the boiling point or melting point, improving the stability, and providing active oxygen to assist the oxidation of the carbon. The main concern from the sensitivity standpoint is whether the $\text{NO}_2\text{-NF}_2$ compounds are more sensitive than the corresponding NF_2 molecules. From the results of this survey and the results of tests at SRI, it appears that the NO_2 group does not intensify the sensitivity of a difluoroamino compound. Sensitivity of the NF compounds seems to be determined mostly

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Table III
SENSITIVITY DATA OF SOME TRIS-DIFLUOROAMINO METHYL COMPOUNDS

Compound No.	Structure	Impact Sens. 50%	Static	Thermal Stability	Other
30	$\text{FC}(\text{NF}_2)_3$	65-70 cm; NE=120		DTA: Exo, 251°	Wenograd: Temp, 250μsec, 520°
96	$[(\text{NF}_2)_3\text{CNH}-]_2\text{CO}$	38 kg cm/2 kg wt; PETN=116 kg cm	pos., 0.02 joule	DTA: Exo, 170°	
153	$[(\text{NF}_2)_3\text{CNHCO-}]_2\text{NH}$	15 kg cm		DTA: Exo, 90° to 100°	
95	$(\text{O}_2\text{N})_2\text{CFCH}_2\text{OC}(\text{NF}_2)_3$	9 kg cm	Neg at .96 joules	toignition, 5 sec, 230° VTS: 0-1cc/g/100h at 60°	Friction Screw pos. at hardness 5
175	$\text{O}_2\text{NOCH}_2\text{CH}(\text{ONO}_2)-\text{CH}_2\text{OC}(\text{NF}_2)_3$	4 kg cm		DTA: Explodes at 150°; Decomp after 132° VTS: 1.8cc/g/100h at 60°	Friction Screw pos. at hardness 5.5
94	$(\text{O}_2\text{N})_3\text{CCH}_2\text{OC}(\text{NF}_2)_3$	7.5 kg cm		Autoignition: 5 sec, 230°	
234	$(\text{F}_2\text{N})_3\text{COCH}_2\text{CH}_2\text{N}-(\text{NO}_2)\text{CH}_2\text{C}(\text{NO}_2)_3$	2.3 kg cm	Neg. at 1.0 joule	VTS: 0.1cc/g/100h at 75° VTS: 9.0cc/g/100h at 90° Autoignition: 5 sec, 230°	Friction Screw neg at hardness 10

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Table III
SENSITIVITY DATA OF SOME TRIS-DIFLUOROAMINO METHYL COMPOUNDS

Compound No.	Structure	Impact Sens. 50%	Static	Thermal Stability	Other
96	$[(F_2N)_3CNH-]_2CO$	12 kg cm	Pos at .015 joule	DTA: Exo, 140° and 170°	Friction Screw pos at hardness 4
294b	$[(F_2N)_3COCH_2CH_2-]_2$	6 kg cm			
382b	$(F_2N)_3CO(CH_2)_8OC-(NF_2)_3$	4.5 kg cm			
228	$(F_2N)_3COCH_2C(NO_2)_2-CH_2OC(NF_2)_3$	5 kg cm		DTA: Explodes at 212° VTS: 5.7cc/g/6 days at 60°	
273	$[(F_2N)_3COCH_2CH-(ONO_2)-]_2$	5 kg cm; NG=15 kg cm	Neg at 1.8 joules		Friction Screw pos with no grit
340	$[(F_2N)_3COCH_2]_2C-CH_2(ONO_2)_2$	5 kg cm	Neg at 1.8 joules	VTS: 0.7cc/g/100h at 60° VTS: 19.3cc/g/100h at 90°	Friction Screw pos at hardness 4
336	$[(F_2N)_3COCH_2]_2CHN-(NO_2)CH_2C(NO_2)_3$	13 kg cm	Pos at .02 joules	VTS: 0.3cc/g/100h at 60° VTS: 9.2cc/g/74h at 90°	Friction Screw pos at hardness 4
356	$[(F_2N)_3COCH_2C-(NO_2)_2CH_2-]_2$	8.5 kg cm	Neg at 1.8 joules	VTS: 0.3cc/g/600h at 60°	Friction Screw pos at hardness 4
330b	$[(F_2N)_3CNHCO-CH_2-]_2C(NF_2)_2$	28 kg cm			

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Table III
SENSITIVITY DATA OF SOME TRIS-DIFLUOROAMINO METHYL COMPOUNDS

Compound No.	Structure	Impact Sens. 50%	Static	Thermal Stability	Other
332	$[(F_2N)_3COCH_2-]_3C-NO_2$	5 kg cm	Pos at .79 joules	DTA: Exo, 225° Autoignition: 5 sec, 234°	
370	$C[-CH_2OC(NF_2)_3]_4$	< 1 kg cm			

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by total energy of the molecule or estimated roughly by the ratio of NF_2 to carbon. Actually, in some cases the presence of nitro groups has improved the sensitivity characteristics of the compound over those that would be expected of a purely NF compound. Examples of this effect will be cited below, although it should be noted that not enough data exist to confirm whether one can design an energetic $\text{NO}_2\text{-NF}_2$ compound that is not excessively sensitive. Data are summarized in Table IV.

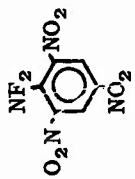
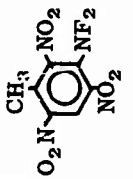
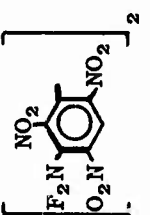
Data on three general classes of $\text{NO}_2\text{-NF}_2$ compounds have been reported: (1) nitrate esters; (2) N-NO_2 ; and (3) carbon-nitro. Nitrate esters, as in their nitroglycerin analogs, are generally quite sensitive (more so than nitroglycerin and RDX). The nitrate compounds are unstable in some configurations, but in general the data from DTA and autoignition tests indicate that as a group they are not unusually unstable. Almost without exception, nitramine compounds are more sensitive to impact than nitroglycerin or RDX. Not enough data were reported to indicate whether these compounds were friction- or static-sensitive. Reports on the stability of the secondary nitramines indicate that the stability characteristics depend somewhat on the configuration of the NF_2 -carbon part of the molecule. Analogous secondary nitramines in the explosives field are known to be quite stable. The instability of a primary nitramine group probably contributes to the general instability of NF_2 -substituted derivatives. The NF_2 -primary nitramines, such as BEDNA (83), are invariably unstable.

Some examples of aliphatic $\text{NO}_2\text{-NF}_2$ are not particularly sensitive. The solid compound 1,1,1,7,7,7-hexanitro-4,4-bis(difluoroamino)heptane, HDFH (337), has sensitivity about that of RDX. This result seems to be an exception to the general effect of geminate groups in imparting sensitivity to a molecule and should be checked. Another example which is an exception to the geminate NF_2 trend is 2,2-bis-(difluoroamino)-5,5-dinitrohexane (306), which also seems to have about the sensitivity of RDX. However, 1,1,1-trinitro-2,2-bis(difluoroamino)-pentane (236) is quite sensitive to the impact and Wenograd tests. The corresponding aliphatic unnitrated NF_2 compound would be relatively sensitive. Tris (difluoroamino) methoxy compounds are discussed above.

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Table IV
SENSITIVITY DATA OF SOME NITRO-NF₂ AND GUANIDINE NF₂ DERIVATIVES

Compound No.	Structure	Impact Sens. 50%	Static	Thermal Stability	Other
Nitro-NF ₂					
83	$[O_2NNHCH(NF_2)-]_2$	10-15 kg in		DTA: Exo, 113°	
337	$[(O_2N)_3CCH_2CH_2-]_2-$ $C(NF_2)_2$	125 kg cm; RDX=150 kg cm		DTA: Exo, 150°	
306	$CH_3C(NO_2)_2CH_2CH_2C-$ $(NF_2)_2CH_3$	> 80 kg cm; RDX=150 kg cm		DTA: Exo, 202°	
236	$(O_2N)_3CCH_2CH_2C-$ $(NF_2)_2CH_3$	15 kg cm; RDX=150 kg cm		Wenograd: 250μsec delay, 458°	
173	$(O_2N)_3CCH_2CH_2CH-$ $(NF_2)_2$	4 kg cm	Pos at 0.05 joule	DTA: Exo, 210°	
264		42 cm/2 kg; HMX=33 cm/ 2 kg	Pos at 0.045 joule	DTA: Exo, 203°	
325		35 cm/2 kg; HMX=33 cm/ 2 kg		DTA: Exo, 195°	
387		4 cm/2 kg; HMX=36 cm/ 2 kg			

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Table IV
SENSITIVITY DATA OF SOME NITRO-NF₂ AND GUANIDINE NF₂ DERIVATIVES

Compound No.	Structure	Impact Sens. 50%	Static	Thermal Stability	Other
<u>Guanidine</u>					
26	FN=C(NF ₂) ₂	0.1 kg cm 50 cm/3 kg	Sens.	DTA: Exo, 243° DTA: Exo, 227°	Shock sens.
59	(F ₂ N) ₂ CFNCF(NF ₂) ₂	14 cm/2 kg			

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In a series of experiments on butanes in which only the NO_2 and NF_2 substituents are varied, little sensitizing contribution by the NO_2 group is found in impact tests. The compound 1,1-bis(difluoroamino)-4,4,4-trinitrobutane (173) is much less spark-sensitive when compared to 1,1-DP (125) and thus does not agree with much of the data on the geminate group sensitizing effect.

The few aromatic NO_2 - NF_2 compounds tested show no unusual sensitivity. Fluorinated picramide (264) had sensitivity values equivalent to RDX. 3-Difluoroamino-2,4,6-trinitrotoluene (325) has similar values but of course is much more sensitive and energetic than TNT.²⁸⁵ By the impact sensitivity test, fluorinated DIPAM (387) is much more sensitive than HMX, but we have found it easy to handle.²⁸⁵ Its spark sensitivity and that of FPIC are very moderate.

8. Guanidine Derivatives

Completely fluorinated guanidine, PFG (26), is an extremely sensitive molecule and has contributed to several accidental explosions in the laboratory and pilot plant. It can be initiated easily by shock, spark, or impact. Other guanidine derivatives have similar severe sensitivity characteristics. The compound F_{11}BG (59) exploded when touched during a sampling action.¹⁵⁵ It and other compounds in the high nitrogen series have sensitivity characteristics similar to those of PFG. Other compounds in a urea series prepared at ICI were more sensitive than nitroglycerin. Both cyclic and straight-chain examples were thermally stable generally.²⁴³

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9. Summary

Valid relationships between the structures of NF compounds and the sensitivity characteristics are discernible. Generally as the energy of the compound increases, the sensitivity problem becomes more severe. The compounds can be divided roughly into three classes: (1) the relatively insensitive compounds, substituted with a low ratio of NF_2 groups to carbon; (2) the compounds with substitution in a ratio of up to one NF_2 group per carbon, possessing high energy, and exhibiting sensitivity characteristics about that of nitroglycerin or HMX; and (3) the ultra sensitive compounds, of very high energy, which are more sensitive than nitroglycerin and HMX and are difficult to desensitize. Much of the desensitization work reported has shown that dilution of an NF compound is the most effective way to reduce its hazard, but the desensitization is sometimes accompanied by excessive loss of energy.

Sensitivity characteristics of the various classes of NF compounds can be correlated with the number and position of the NF_2 groups on the carbon chain, and some types of substitution are particularly sensitive to certain methods of energy input; e.g. to spark initiation or to friction. The general sensitivity of a compound is established by the NF_2 substitution and is usually not intensified by the effect of other oxidizing groups such as nitro or nitrate.

Sensitivity properties of the alkanes generally reflect the properties which can be expected of other classes such as the alcohols, esters, or ethers. Distinct substitution effects are discernible in the alkanes and can be summarized as follows:

- (1) Vicinal substituted compounds of a ratio of about two NF_2 groups to three carbon atoms are in the nitroglycerin sensitivity range.
- (2) Geminate NF_2 groups impart more sensitivity to a compound than do the vicinal group, particularly when the geminate group is terminal, as in the 1,1 position. Desensitization

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of geminate compounds by increasing the carbon content is ineffective. Generally the energetic geminate compounds are in the nitroglycerin sensitivity range and appear especially susceptible to spark and shock initiation.

- (3) Separation of NF_2 groups by one or more CH_2 groups appears to make the compounds less sensitive.
- (4) Increasing the degree of substitution in a carbon chain does not intensify sensitivity properties.
- (5) Alkanes, and probably other similarly substituted classes, are susceptible to initiation by low energy input and can propagate by a destructive low velocity detonation wave.

In alcohols there is no discernible effect by the hydroxyl group. However esters appear to be less sensitive than the parent alcohols, possibly because of a large drop in energy. Ethers possess the properties of the parent NF substituted hydrocarbon moiety; the energetic compounds are as sensitive as nitroglycerin or more so. In cyclic compounds, alkyl halides, cyanides, isocyanates there also is no discernible structural effect of the functional groups. The sensitivity of these compounds is equivalent to the parent alkanes.

Tris(difluoroamino)methyl and methoxy compounds are in the ultra-sensitive range, being more sensitive than nitroglycerin or HMX and possessing many cases extreme sensitivity characteristics toward any method of energy input. As in the geminate series diluting a tris(difluoroamino)methoxy group by additional methylene groups does not obviate the effect of the tris methyl substitution. Attempts to desensitize this class of compounds by conventional means were unsuccessful, leaving the compound several orders of magnitude more sensitive than conventional handleable propellant or explosive ingredients.

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B. Sensitivity Characteristics According to Test Method

Following are a few tables which were made up to illustrate how specific test results cannot be correlated with results from a test using a different mode of energy input. Thus, a single test cannot define the general sensitivity of a compound. The first table, V, summarizes the impact sensitivities of several types of bis, tris, tetrakis, and other NF_2 compounds compared with the value of a standard. The energetic NF compounds are quite sensitive relative to standard compounds. However direct quantitative comparisons should be avoided, since the physical state of the test compound and the standard may be different, e.g. solid RDX compared with a liquid NF compound.

In Table VI, some compounds are listed in order of static sensitivity. The static equivalent value for man is 10,000 MEV (man equivalent volts). Thus all compounds having a static sensitivity value close to this number are probably too dangerous to handle. Upon comparing static test results with the data from the mild 8.3 gm ball drop test (in which all positive tests show sensitivity greater than nitroglycerin or RDX), several are noted which are quite ball drop sensitive but are not particularly static sensitive. A third table, VII, shows some compounds in decreasing ball drop values which are not paralleled by either spark sensitivity or impact test values.

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Table V
SELECTED NF COMPOUNDS - RESULTS OF
IMPACT SENSITIVITY TESTS VERSUS STANDARD VALUES

Compound No.	Structure	Machine	Impact Sens	Standard Value	Reference
<u>Bis NF₂</u>					
67	CH(NF ₂) ₂ CH(NO ₂) ₂	Picatinny	1 cm/2 kg	RDX = 30-35 cm/2 kg	5
80	F ₂ NCH ₂ CH ₂ NF ₂	Picatinny	11 kg in	RDX = 20 kg in	88
109	C ₂ NOCH ₂ C(NF ₂) ₂ CH ₂ ONO ₂	Picatinny	1-2 kg in		97
113	F ₂ NCH ₂ CH(NF ₂)CH ₂ Br	Picatinny	8 kg in	RDX = 20 kg in	88
126	CH ₃ CH(NF ₂)CH ₂ NF ₂	Picatinny	14 kg in	RDX = 20 kg in	88
128	CH ₃ C(NF ₂) ₂ CH ₃	Picatinny Olin	2.8 in/1 kg w >12 in/1 kg	RDX = 10 in/1 kg Propylnitrate = 4 in/1 kg	178 178
188	HOOCCH ₂ CH(NF ₂)CH ₂ NF ₂	Picatinny	35 kg in	RDX = 15.5 kg in	80
206	F ₂ NCH ₂ C(NF ₂)(CH ₃)CH ₂ ONO ₂	Picatinny	5.6 kg in	RDX = 20 kg in	180
236	(O ₂ N) ₃ CCH ₂ CH ₂ C(NF ₂) ₂ CH ₃	Olin	15 kg cm	RDX = 150 kg cm	154
281	CH ₂ =CHCOOCH ₂ CH(NF ₂)CH ₂ NF ₂	Picatinny	>38 in/1 kg	NG = 10.7 in/1 kg	198
306	CH ₃ C(NO ₂) ₂ CH ₂ CH ₂ C(NF ₂) ₂ CH ₃	Olin	>80 kg cm	RDX = 150 kg cm	154
337	(O ₂ N) ₃ C(CH ₂) ₂ C(NF ₂) ₂ (CH ₂) ₂ - C(NO ₂) ₃	Olin	125 kg cm	RDX = 150 kg cm	154
<u>Tris NF₂</u>					
30	FC(NF ₂) ₃		70-65 cm	NG = >120 cm	86
137	(F ₂ N) ₃ COCH ₂ CH ₂ NH ₃ ClO ₄		8.6 cm/2 kg	NG = 11-13 cm/2 kg HMX = 51 cm/2 kg	240 240
284	(F ₂ N) ₃ COCH ₂ C(CH ₂ ONO ₂) ₃	Bruceton	2.0 kg cm	NG = 10.0 kg cm	111

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Table V
SELECTED NF COMPOUNDS - RESULTS OF
IMPACT SENSITIVITY TESTS VERSUS STANDARD VALUES

Compound No.	Structure	Machine	Impact Sens	Standard Value	Reference
Tetrakis NF ₂					
59	(F ₂ N) ₂ CFNCF(NF ₂) ₂	Picatinny	12-14 cm/2 kg	NG = >120 cm/2 kg	86
270	$\begin{array}{c} F_2NCH-C(NF_2) \\ \\ F_2NCHOC(NF_2)COCH_3 \end{array}$		~1 kg in	RDX = 20 kg in	88
>Tetrakis NF ₂					
294a	[F ₂ NCH ₂ CH(NF ₂)CH(NF ₂)-] ₂ O	BuMines Bruceton	2-4 cm/2 kg 2.3 kg cm	NG = >100 cm/2 kg NG = 10.0 kg cm	20 111
366	[F ₂ NCH ₂ C(NF ₂) ₂ -](-CH ₂) ₄	Picatinny	5-6 kg in	RDX = 10 kg in	184
377	$\begin{array}{c} [F_2NCH_2CH(NF_2)OCH_2-]_4- \\ \\ CHOCH(NF_2)CH_2NF_2 \end{array}$	Picatinny	11 kg in	NG = 11 kg in	191

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Table VI
SELECTED NF COMPOUNDS
IN ORDER OF DECREASING STATIC SENSITIVITY

Compound No.	Structure	DuPont Static Test MEV at deton.	DuPont Ball Drop, in. with 8.3 gm ball
80	$F_2NCH_2CH_2NF_2$	~8,200	<35 in
247	$[F_2NCH_2CH(NF_2)-CH_2$	10,950	Detonate at 40
287	$F_2NCH_2CH(NF_2)CH(NF_2)-CH(NF_2)OOCCH_3$	13,700	Negative at 45
108	$F_2NCH_2CH(NF_2)N(NO_2)-CH=O$	14,680	Detonate at 10
249	$[F_2NCH_2CH(NF_2)O-]_2CH_2$	18,250	Detonate at 26
126	$CH_3CH(NF_2)CH_2NF_2$	25,600	Negative at 45
81	$F_2NCH_2CH(NF_2)NHNO_2$	33,600	Negative at 10 Shot at 12 in
158	$F_2NCH=CHNF_2$	36,400	Negative at 45
120	$F_2NCH_2CH(NF_2)CH_2ONO_2$	36,500	Negative at 20 Shot at 22 in
106	$F_2NCH_2CH(NF_2)OOCH$	38,400	
193	$F_2NCH_2CH(NF_2)CH(ONO_2)-CH_2ONO_2$	41,600	Negative at 22 Shot at 26 in

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Table VII
SELECTED NF COMPOUNDS
IN ORDER OF DECREASING SENSITIVITY TO DU PONT
FALL TEST, HEIGHT WITH 8.3 GM BALL

Compound No.	Structure	DuPont Ball Drop, in. with 8.3 gm ball	Static Sens M.E.V.	Impact, 50% Point
199	$[F_2NCH_2CH(NF_2)]_2-O$	Negative at 8	Negative at 28,300	6 kg cm
195	$[O_2NOCH_2CH(NF_2)]_2$	Detonated at 10		3 kg cm
108	$F_2NCH_2CH(NF_2)N(CHO)NO_2$	Detonated at 10	Detonated at 14,680	2.5 kg cm
81	$F_2NCH_2CH(NF_2)NHNO_2$	Negative shot at 12	Detonated at 33,600	11 kg cm
120	$F_2NCH_2CH(NF_2)CH_2ONO_2$	Negative at 20 Shot at 22	Detonated at 36,500	2 in/2 kg
193	$F_2NCH_2CH(NF_2)CH(ONO_2)CH_2ONO_2$	Negative at 22 Shot at 26	Detonated at 41,600	8 kg cm
249	$[F_2NCH_2CH(NF_2)O]_2CH_2$	Detonated at 26	Detonated at 18,250	11 kg cm
80	$F_2NCH_2CH_2NF_2$	Detonated at <35	Detonated at ~18,200	2 in/5 kg
247	$[F_2NCH_2CH(NF_2)]_2CH_2$	Detonated at 40	Detonated at 10,950	16 kg cm

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C. The Thermal Decomposition of NF Compounds

1. Introduction

The kinetics and mechanism of the thermal decomposition of several NF compounds have been studied in connection with the thermal sensitivity, detonation phenomena, and possible desensitization of this general class of compounds. From an understanding of the chemical processes involved in the thermal decomposition of a compound under mild temperature and pressure conditions where explosions do not occur, certain extrapolations could be made to more severe conditions where explosions do occur, possibly providing some insight into the chemical mechanisms of initiation and propagation of explosion in the compound. A knowledge of the chemical reactions leading to such an explosion could indicate what steps should be taken to desensitize the material by inhibiting or arresting these reactions.

This review covers the literature to date on the kinetics and mechanism of the thermal decomposition of NF compounds: gases, liquids, solutions, and solids.* Only homogeneous reactions initiated by heat and run under controlled conditions are discussed. In general, NF compounds are quite surface sensitive; consequently much work has been complicated by wall reactions, particularly dehydrofluorination. Such apparent heterogeneous, catalyzed reactions have not been included in this survey.

*The small superscript numbers in the text refer to the numbers in the Reference Index.

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2. Activation Parameters for Thermal Decomposition

All available activation parameters for the homogeneous thermal decompositions of NF compounds have been summarized in the table below. Again, apparent heterogeneous or catalyzed decompositions have not been included. As indicated in the table, these activation parameters have been obtained from (a) direct thermal decomposition measurements; (b) the temperature at which the compound is half decomposed, $T_{1/2}$; (c) autoignition tests; (d) adiabatic self-heating experiments; or (e) explosion limit data. In general, the reactions were followed by observation of the change in pressure with time or the disappearance of starting material with time. Where the values obtained for any one compound at one laboratory are consistent, only the more recent reference is cited. More than one entry per compound for a given laboratory does not necessarily mean that the parameters were redetermined experimentally, but may mean that they may have been recalculated from the data. Correlations between thermal stability and activation energy are pointed out in Section III-B-3. However, numerical values of activation parameters are not always repeated in that section.

Kinetic studies on the thermal decomposition of NF compounds show that the reactions often proceed by initial unimolecular homolytic bond cleavage. Pre-exponential factors of 10^{14} - 10^{16} sec^{-1} are typical for such reactions, and these A factors can serve as criteria for this type of mechanism. The activation energies for thermal decompositions with A factors falling in this range are probably the most reliable, and also more nearly represent the strength of the bond being broken in the initial homolysis when this step is rate-determining. An A factor falling outside this range would most likely indicate a different or mixed decomposition pathway. Apparent activation energies for branched-chain reactions are typically much lower than the strengths of any of the bonds being broken. When the activation energies vary drastically over a temperature range, it is a good indication that the observed reaction is partly homogeneous and partly heterogeneous. This apparently accounts for some of the variation in data for some compounds listed in the table. Variations are also due in part to the methods used in obtaining the data. The results from adiabatic self-heating experiments and from autoignition tests are not always consistent and appear less reliable.

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Table VIII

ACTIVATION PARAMETERS FOR THE HOMOGENEOUS DECOMPOSITION
OF NF COMPOUNDS^a

Compound	E_a kcal mole ⁻¹	A sec ⁻¹	Phase	Temperature Range, °C	Condition ^b	Laboratory ^c	Reference ^d
$\text{FN}=\text{CFNF}_2$ Code Name: PFF Compound No.: 21	49.3	$10^{15.2}$	gas	400-477	flow	Rocketdyne	171, 264
$\text{FN}=\text{C}(\text{NF}_2)_2$ Code Name: PFG Compound No.: 26	52.9	$10^{15.8}$	gas	above 400	flow	Rocketdyne	170, 171
$\text{F}_2\text{C}(\text{NF}_2)_2$ Code Name: H Compound No.: 27	53.6	$10^{15.7}$	gas	370-460	flow	Rocketdyne	166
$\text{FC}(\text{NF}_2)_3$ Code Name: R Compound No.: 30	45.8 43.1 45.8 48.5 47.6 48.3	4.9×10^{18} 10^{14} 10^{15} $10^{16.7}$ $10^{16.6}$ $10^{16.4}$	gas gas gas gas gas gas	225-250 225-250 225-250 253-377 250-350 250-380	static static static flow flow flow	3M 3M 3M Rocketdyne Rocketdyne Rocketdyne	140, 143 244 242 164 259, 260 166
$\text{C}(\text{NF}_2)_4$ Code Name: T, Δ, delta Compound No.: 31	38.6 42.5 40.4	4×10^{15} $10^{16.1}$	gas gas gas	150-175 160-190 190-250	static static flow	Am. Cy. Dow Rocketdyne	42, 260 260 165, 166 259, 260
$(\text{F}_2\text{N})_3\text{CNH}_2$ Code Name: Tris-A Compound No.: 45	29.6	$10^{11.7}$ $\Delta S^\ddagger = -5.92 \text{ eu.}$	gas	185-205	static	Am. Cy.	264
$(\text{F}_2\text{N})_3\text{COCH}_3$ Code Name: Tris-E Compound No.: 75	~30	10^{11}	gas	~150-200	static	Am. Cy.	264
$(\text{F}_2\text{N})_3\text{CNHCONH}_2$ Code Name: Tris-U Compound No.: 76	30	2×10^{13}	solid	90-130	static	NOTS	264
$(\text{F}_2\text{N})_3\text{CNHCONHC}(\text{NF}_2)_3$ Code Name: DTU Compound No.: 96	24 21.7	10^9 10^7 $\Delta S^\ddagger = -24.7 \text{ eu.}$	solid solution	130-150 100-150	static halocarbon oil plus 1-3% diglyme	NOTS Am. Cy.	265 260

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Table VIII
ACTIVATION PARAMETERS FOR THE HOMOGENEOUS DECOMPOSITION
OF NF COMPOUNDS^a

Compound	E _a kcal mole ⁻¹	A sec ⁻¹	Phase	Temperature Range, °C	Conditions ^b	Laboratory ^c	Reference ^d
CH ₃ CH(NF ₂)CH ₂ NF ₂ Code Name: 1, 2-DP Compound No.: 126	57.3 64.2 51	10 ^{16.9} 10 ¹⁵	gas liquid gas	430-501 170-207 25-1000	flow A.S.H. flow, T ₁ 2 flow, T ₁ 2	Rocketdyne SRI SRI SRI	165, 259 214 220 220
CH ₃ C(NF ₂) ₂ CH ₃ Code Name: 2, 2-DP Compound No.: 128	53.4 52.0 46.5 38.4	1.6 x 10 ¹⁸ 10 ^{15.7} 5.3 x 10 ¹²	liquid gas gas gas	196-220 292-334 248-275 276-304	A.S.H. static static, thermal static thermal expl. L flow, T ₁ 2 flow, T ₁ 2	SRI ARC ARC ARC ARC SRI SRI	213 46, 262 51 49 48 220 220
(F ₂ N) ₃ COCH ₂ CH ₂ NH ₃ ⁺ ClO ₄ ⁻ Code Name: INFO 635P Compound No.: 137	51 45.3	5 x 10 ²⁰ 10 ¹⁷	solid solid	160-210 160-210	static static	NOTS NOTS	260 260
F ₂ NCH ₂ C(CH ₃) ₂ (NF ₂) Code Name: IBA Compound No.: 213	25-47 51.6 47.0 53.0	10 ¹⁵ 10 ¹⁷	liquid liquid gas gas	~ 140-175 148-175 25-1000 25-1000	A.S.H. A.S.H. flow, T ₁ 2 flow, T ₁ 2	SRI SRI SRI SRI	213 214 220 220
(CH ₃) ₃ CNF ₂ Compound No.: 221a	29.2 ^e	ΔS [‡] = -6.8 e.u.	gas	150-450	flow	R and H	196
FN=N(O)C(CH ₃) ₂ CH(NF ₂)CH ₃ Compound No.: 253	33.6 ^e	ΔS [‡] = 7.2 e.u.	gas	115-145	static	R and H	194
(F ₂ N) ₃ COCH ₂ CH ₂ CH ₂ OC(NF ₂) ₃ Code Name: FA-BDE Compound No.: 272a	31.9 45.5 51.4 44.0 35.5 20	1.3 x 10 ¹¹ 2.3 x 10 ¹⁶ 3.0 x 10 ¹⁸ 3.1 x 10 ¹² 3.7 x 10 ⁶	liquid liquid liquid liquid liquid liquid		autoig. autoig. autoig. autoig. autoig. autoig.	Esso Esso Esso Esso Esso Esso	264 115 115 116 116 117

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Table VIII
ACTIVATION PARAMETERS FOR THE HOMOGENEOUS DECOMPOSITION
OF NF COMPOUNDS^a

Compound	E _a kcal mole ⁻¹	A sec ⁻¹	Phase	Temperature Range, °C	Conditions ^b	Laboratory ^c	Reference ^d
$[(F_2N)_3COCH_2CH_2CH_2OC(NF_2)_3]_2$ Code Name: Poly FA-BDE Compound No.: 272b	46 34.6 25.3 24.2	2.5×10^{11} 9.5×10^7 2×10^7	solid solid solid solid		static autoig. autoig. autoig.	Dow Esso Esso Esso	64 264 116 117
$[(F_2N)_3COCH_2CH_2OC(ONO)_2]_2$ Code Name: FA-BDN Compound No.: 273	41.0 36.0 40.9	3.1×10^{14} 1.8×10^{12} 3.1×10^{14}	liquid liquid liquid		autoig. autoig. autoig.	Esso Esso Esso	264 116 117
$(O_2NOCH_2)_3CCH_2OC(NF_2)_3$ Code Name: FA-PETRIN Compound No.: 284	35.7	5.7×10^{12}	liquid		autoig.	Esso	264
$[F_2NC_6H_4CH(NF_2)CH(NF_2)]_2O$ Code Name: HPE Compound No.: 294	35-38 35.6	10^8-10^{10} 4.2×10^8	liquid liquid		autoig. autoig.	Esso Esso	117 116
$[(F_2N)_3COCH_2CH(OH)]_2$ Code Name: FA-BDG Compound No.: 295	22.1 23-36 34.5	1.6×10^7 10^7-10^{12} 3.4×10^{11}	solid solid solid		autoig. autoig. autoig.	Esso Esso Esso	116 117 264
$O_2NOCH_2C[CH_2OC(NF_2)_3]_3$ Code Name: FA-PEMON Compound No.: 357	37.2	3.1×10^{13}	liquid		autoig.	Esso	117, 264

- a. E_a = activation energy. A = pre-exponential factor.
b. Static = static reactor. Flow = flow reactor. A.S.H. = adiabatic self-heating. T_{1/2} = temperature at which compound half decomposed. Autoig = autoignition. Expl L. = Explosion limits.
c. Am. Cy. = American Cyanamid Company, SRI = Stanford Research Institute, R and H = Rohm and Haas, ARC = Atlantic Research Corporation, NOTS = Naval Ordnance Test Station.
d. Numbers refer to Reference Index.
e. ΔH[‡] value, not E_a.

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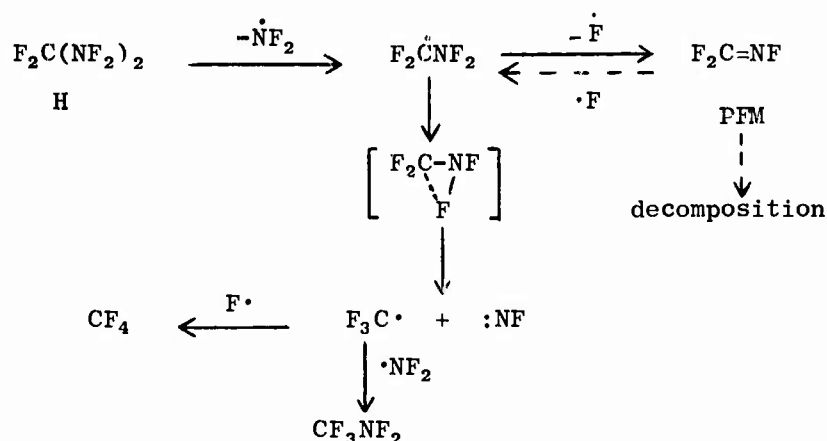
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3. Kinetics and Mechanism of Thermal Decomposition

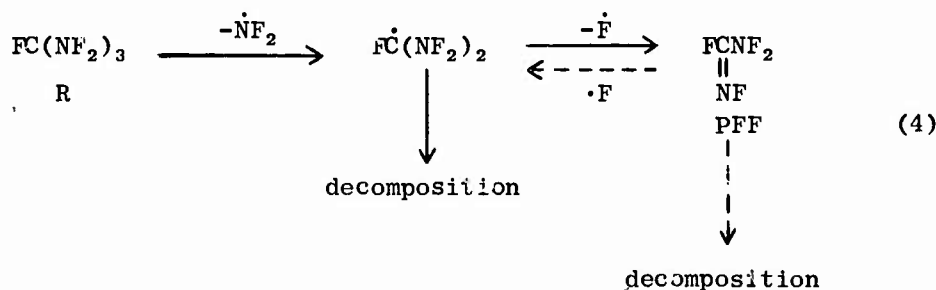
a. Perfluorodifluoroaminomethanes. The kinetics of the lowest member of this series, CF_3NF_2 , have not been studied. However, the carbon-nitrogen bond energy in this compound was determined by electron impact to be $59.7 \text{ kcal mole}^{-1}$ by Rohm and Haas. The other members of this series, $\text{CF}_2(\text{NF}_2)_2$, $\text{CF}(\text{NF}_2)_3$, and $\text{C}(\text{NF}_2)_4$, have been studied at several different laboratories.

The gas phase thermal decomposition of $\text{F}_2\text{C}(\text{NF}_2)_2$, Compound H, has been studied by Rocketdyne^{166,244,259,260} in a monel stirred-flow reactor. Using helium as a carrier gas, the total pressure was approximately one atmosphere and the partial pressure of H was 2 to 10 mm Hg. Over the temperature range $370\text{--}460^\circ\text{C}$, the decomposition was homogeneous and first-order in H. The major products were N_2 , NF_3 and CF_4 ; CF_3NF_2 was a minor product. One-half mole of nitrogen was produced for each mole of starting material. Two intermediates, N_2F_4 and $\text{F}_2\text{C}=\text{NF}$ (PFM), were also observed to build up and then decrease during the course of the decomposition. The pre-exponential factor ($10^{15.7} \text{ sec}^{-1}$) and activation energy ($53.6 \text{ kcal mole}^{-1}$) are consistent with an initial, rate-determining, homolytic, carbon-nitrogen bond cleavage. The resultant carbon radical then decomposes both to trifluoromethyl radicals, presumably in a concerted intramolecular reaction, and also to PFM. The mechanism of decomposition of PFM is not known, but it could add a fluorine atom and return to the carbon radical or decompose directly to products. These reactions are summarized below:

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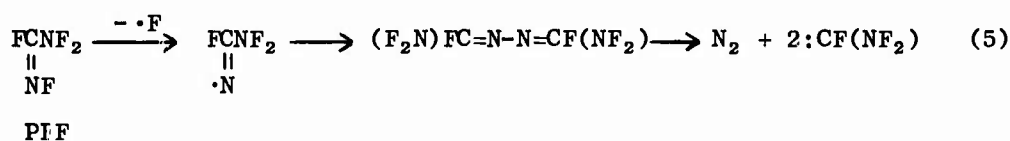
Rocketdyne^{164-166,244,259,260} also studied the decomposition of Compound R, $\text{FC}(\text{NF}_2)_3$, in the monel stirred-flow reactor with helium carrier gas under the same pressure conditions given for H. Compound R decomposed at lower temperatures than H, and the reaction was homogeneous from 253-377°C. The major products, N_2 , NF_3 , and CF_4 , were the same as those from H and were formed in the ratio of 1:1:1. One mole of R produced one mole of nitrogen. The minor product was still CF_3NF_2 , but there were three intermediates: $\text{FN}=\text{CFNF}_2$ (PFF), $\text{F}_2\text{C}=\text{NF}$ (PFM), and N_2F_4 . More PFF was formed from R than PFM from H. The initial rate-limiting step in the decomposition of R also appeared to be unimolecular homolytic carbon-nitrogen bond cleavage; the resultant carbon radical could decompose directly or go to PFF.



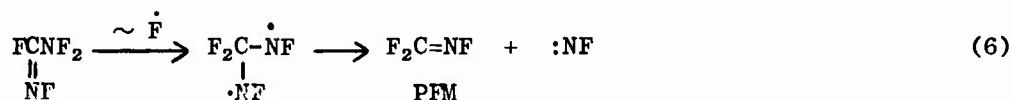
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Equations 1, 2, and 3 also account for products. Since additives N_2F_4 , F_2 , O_2 , $C(NO_2)_4$, N_2O_4 , and NO did not affect the rate of decomposition of R, but did affect the final product distribution, the decomposition was presumed to be a nonchain radical sequence.

The decomposition of the intermediate PFF was also investigated by Rocketdyne^{171,264,288} using the same flow reactor and pressure conditions given for compounds H and R. This decomposition was studied over the temperature range of 358-477°C. Below 400° the reaction was heterogeneous; above 400° it was unimolecular and homogeneous. The major products from the homogeneous reaction were N_2 (very high yield), CF_3NF_2 , CF_4 , PFM, and an unknown. The lack of production of NF_3 and N_2F_4 indicated that $\cdot NF_2$ radicals were not formed during the decomposition of PFF. The addition of N_2F_4 to the reaction mixture, presumably under homogeneous conditions, resulted in formation of large quantities of NF_3 , showing the presence of fluorine radicals (Eq. 2). Since a nitrogen-fluorine bond is more easily broken than a carbon-fluorine bond, the following possible decomposition pathways have been suggested:



and/or



Over the temperature range where the decomposition of R was studied, the decomposition of the intermediate PFF should be predominantly heterogeneous. The products from the heterogeneous reaction of PFF apparently were not determined and it is not clear whether the mechanisms outlined in Eqs. 5 and 6 would apply to the heterogeneous reaction. Since fluorine atoms are present in the decomposition of R, PFF could also possibly decompose by the reverse of Eq. 4 during this reaction.

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Minnesota Mining and Manufacturing Company (3M)^{143,242,244} has also studied the gaseous decomposition of R over the temperature range 225-250°C, at approximately 700 mm Hg. The reaction was heterogeneous in a stainless steel static reactor, but was predominantly homogeneous in a monel static reactor. The final products, N₂, NF₃, and CF₄, from the homogeneous reaction and their ratios, 1:1:1, were the same as those found by Rocketdyne. 3M found CF₃NF₂, F₂C=NF, and F₂C(NF₂)₂ to be intermediates that built up and then decreased with time. Evidence of a reaction with the reactor wall itself may have accounted for the presence of the last intermediate, Compound H. 3M found some rate acceleration due to the addition of NO, but also concluded that the decomposition proceeded by initial carbon-nitrogen bond homolysis to produce ·NF₂ radicals.

Decomposition of the highest member of this series of perfluoro-difluoroaminomethanes, Compound T, has been studied at a number of different laboratories, including Dow, American Cyanamid, and Rocketdyne. The first of these laboratories decomposed T, C(NF₂)₄, in a static glass and monel reactor.^{60-62,260} The reaction was homogeneous over the temperature range studied, 160-190°C, and first-order in T. The species identified from the reaction were N₂, NF₃, CF₄, (F₂N)FC=NF, and F₂C=NF. The initial step was thought to be a homolytic carbon-nitrogen bond cleavage and subsequent steps might then involve a chain reaction of the resultant ·NF₂ radicals with T and a unimolecular decomposition of the tris(difluoroamino)methyl radical, ·C(NF₂)₃.

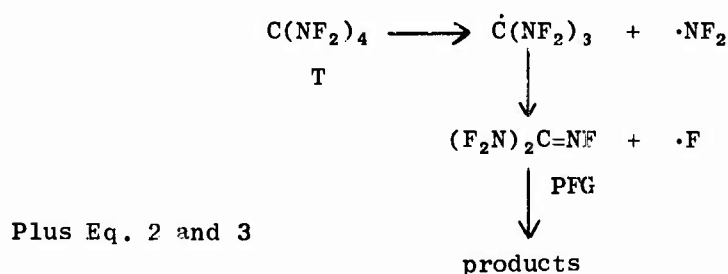
American Cyanamid^{39,42,260} studied the decomposition of T in a static monel reactor at 150-250°C and 40 to 100 mm H₂ pressure. The kinetics for the homogeneous reaction were first-order and the initial step was thought to be the homolytic fission of the carbon-nitrogen bond. The products of the reaction were similar to those reported by Rocketdyne.

The most extensive work with Compound T has been done by Rocketdyne.^{165,166,169-171,259,264,288} Again using the monel stirred-flow reactor, with helium carrier gas at a total pressure of approximately one atmosphere and a partial pressure of T of 2 to 10 mm Hg, this decomposition reaction was studied between 193°C and 254°C. In this

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range, the reaction was homogeneous and unimolecular. The products again were N_2 , NF_3 , CF_4 , and CF_3NF_2 . The yield of nitrogen varied from 0.25 mole N_2 /mole T at 50% reaction to over 2 moles N_2 /mole T at greater than 85% reaction. The intermediates observed were $(F_2N)_2C=NF$ (PFG), $(F_2N)FC=NF$ (PFF), $F_2C=NF$ (PFM), and N_2F_4 . The yield of PFG was fairly high, while those of PFF and PFM were low. The activation parameters ($E_a = 40.4 \text{ kcal mole}^{-1}$, $A = 10^{16.1} \text{ sec}^{-1}$) were consistent with an initial homolytic carbon-nitrogen bond rupture. Since additives N_2F_2 , F_2 , and N_2O_4 did not affect the rate, but affected the product distribution, a nonchain radical mechanism was assumed. Considerably more PFG was formed from T than PFF from R, and more PFF was formed from R than PFM from H. By using a copper tubular reactor, higher temperatures could be attained for the decomposition of T and, under these conditions, the conversion of T to PFG was essentially quantitative. PFG must then decompose to products. The initial steps then in the decomposition of T are:



The decomposition of the intermediate PFG was also investigated by Rocketdyne.^{169-171, 264, 288} From studies in several different reactors, this compound was found to be very surface-sensitive. In the monel stirred-flow reactor, the decomposition of PFG was heterogeneous below 350°C and homogeneous and unimolecular above 400°C. The products and the product distributions from the homogeneous and heterogeneous reactions were very similar. In order of decreasing abundance, the species produced during the reaction were $N_2 > CF_3NF_2 > CF_4 > NF_3 > N_2F_4 > PFF > PFM$, the last three being intermediates. The yield of nitrogen was very high, while the yields of NF_3 , N_2F_4 , and PFF were quite low. At higher temperatures,

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T and PFG gave the same product distribution, except that T gave more NF_3 and N_2F_4 . The low yields of NF_3 and N_2F_4 suggested that the initial step was not a bond homolysis to produce $\cdot\text{NF}_2$ radicals. The addition of N_2F_4 did not affect the homogeneous rate of decomposition of PFG. PFF was some three times more stable than PFG and little PFF was formed in the decomposition of PFG; this indicated that PFF was not a direct product from PFG. Mathematical treatment of the decomposition data for PFG also supported this conclusion. Again the decomposition of PFG was predominantly heterogeneous over the temperature range at which the decomposition of T was studied. Below 200°C in the monel reactor, the heterogeneous decomposition of PFG was faster than the homogeneous decomposition of T. Below 600°C , the homogeneous decomposition of PFG was slower than that of T. The principal exothermic reactions in this latter decomposition of T occur after the formation of PFG.

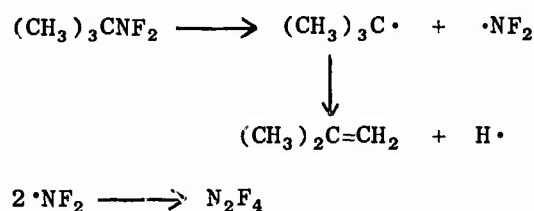
The thermal stabilities of the perfluorodifluoroaminomethanes decrease in the order $\text{H} > \text{R} > \text{T}$. This behavior is reflected in the decreasing activation energies for this series. Since all three compounds decompose by initial unimolecular, rate-limiting, homolytic, carbon-nitrogen bond fission, these activation energies must very nearly represent the C-N bond energies. Replacement of a $-\text{NF}_2$ group by a fluorine then increases the first C-N bond energy by about 6 to 7 kcal mole⁻¹. The bond energy of CF_3NF_2 also falls in line with this correlation. Just the opposite effect occurs for the corresponding double-bond imines. Going from PFG to PFF results in a decrease in activation energy of 3.6 kcal mole⁻¹. However, the initial step or mechanism is not known for the decomposition of these compounds and it is not clear what bond energies these values might represent.

b. Mono-difluoroaminoalkanes. Very little kinetic work has been done on the thermal decomposition of mono- NF_2 compounds. The studies by Rohm and Haas¹⁹² on primary alkyl amines (CH_3NF_2 and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NF}_2$) were complicated by surface reactions and predominantly dehydrofluorination products were observed. The tertiary alkylamine, tert-butyldifluoroamine, has been studied by two laboratories, Stanford Research Institute (SRI) and Rohm and Haas. SRI^{258,266} has studied the thermal

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decomposition of this tertiary-alkylamine in a glass flow reactor with a fused silica reaction chamber. The temperature range, 645-907°C, was covered at pressures of 10^{-3} mm Hg. The major reaction products were isobutylene and N_2F_4 ; 1.5% isobutane and trace amounts of HF and HNF_2 were the minor products. Under the same conditions, tert-butyl radicals, generated from azoisobutane, were shown to give more disproportionation, producing 89% isobutylene and 11% isobutane. The proposed decomposition sequence for the NF_2 compound is



The tert-butyl radical acquires enough energy through subsequent wall collisions to lose the hydrogen atom.

Rohm and Haas^{192, 196, 257, 263} studied the decomposition of this same compound in a monel stirred-flow reactor with helium carrier gas at a total pressure of one atmosphere over the temperature range 150-450°C. The partial pressure of tert-butyldifluoroamine was slightly less than 1 mm Hg. The only product obtained was isobutylene which was present in 25 to 50% yield. No other hydrocarbon, N_2F_2 , N_2F_4 , nor HNF_2 was present. A black deposit was formed during decomposition in the cold, quenching region of the reactor. When pure isobutylene in helium was put through the reactor, no deposit was obtained. In addition, when isobutylene was put through in the presence of HNF_2 , no reaction occurred except decomposition of the HNF_2 . The order of the decomposition of tert-butyldifluoroamine was questionable. Calculated for first-order kinetics, the activation energy was quite low (~ 30 kcal mole⁻¹). This value did not change significantly when calculated for different order kinetics. The decomposition kinetics are probably very complex and not of a simple order. The mechanism may involve a chain process and/or a multicenter elimination. No rate enhancement was observed when the reactor surface area was increased.

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The decomposition of tert-butyldifluoroamine was also studied at Rohm and Haas²⁵⁷ in a static aluminum reactor in the temperature range 100 to 240°C. The pressure of the pure amine varied from 0.2 to 25 mm Hg. After conditioning of the reactor, the yield of isobutylene was 80 to 90%. No deposit was found on the vessel walls. The decomposition was apparently homogeneous; the rate was not proportional to the surface area. Added helium accelerated the decomposition, while excess isobutylene retarded the reaction. The kinetics appeared to be between one-half and first-order. The Rohm and Haas results from the static and flow reactors roughly fall on the same line when plotted as $\log k$ versus $1/T$, for first-order kinetics. Shock tube results from studies recently initiated at Rohm and Haas²⁵⁷ also appear to fall on this same line.

The decomposition results for tert-butyldifluoroamine reported by Rohm and Haas and SRI are quite different. It is apparent, however, that in some way, the NF compound loses the elements of HNF_2 to give isobutylene. The scheme proposed by SRI, in which a $\cdot\text{NF}_2$ radical is initially lost, is consistent with the decomposition pathways found by that laboratory for other bis-alkylamines. SRI apparently is observing the initial bond cleavage and the first products formed in the decomposition. At higher pressures, the reaction becomes more complex and Rohm and Haas perhaps is observing a chain reaction and/or a multicenter elimination. Experiments are under way at both laboratories to establish the existence of a radical chain reaction.

c. Bis-difluoroaminoalkanes. The decomposition of several bis(N,N-difluoroamino)alkanes has been studied in the gas phase, liquid phase, and solution. Without exception, the work on neat liquids, nitrobenzene solutions, and even some static gas systems has been dominated by heterogeneous surface-catalyzed reactions.^{213-216,221} Much useful information, however, has been obtained from gas-phase thermal decomposition studies.

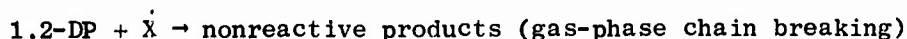
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SRI²¹⁹⁻²²⁴ also examined the decomposition of 1,2-DP using a glass flow reactor, with a fused silica reaction chamber, at pressures of about 10^{-3} mm Hg. A temperature range of 25-1000°C was actually scanned and, under these reaction conditions, 1,2-DP was half-decomposed at 740-750°C. The products of the reaction were CH_3CN , FCH_2CN , HCN , HF (SiF_4), N_2F_4 , $\text{CH}_3\text{CH}=\text{CH}_2$, NF_3 (trace), and $\text{CH}_3\text{C}(=\text{NF})\text{CN}$. The activation parameters ($E_a = 57 \text{ kcal mole}^{-1}$, $A = 10^{17}$ preferred values²²⁰) calculated from $T_{1/2}$ for unimolecular decomposition, and products indicated an initial carbon-nitrogen bond homolysis and the following decomposition mechanism was proposed:



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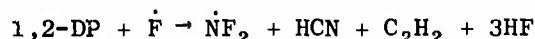
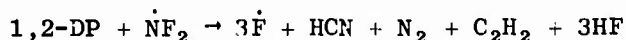
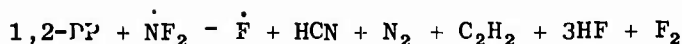
Both the thermal decomposition and explosion of 1,2-DP have been studied by Atlantic Research Corporation (ARC)^{48-52,244,260-262,264,287} in a static pyrex reactor between 250-450°C. The pressures were initially 5 to 45 mm Hg, but now have been extended up to 200 mm Hg. Not only explosion limits, but also the kinetics of the thermal reactions prior to explosion, were studied. Between 250°C and 350°C, the thermal decomposition was heterogeneous and the activation energies were low. Above 350°C, the reaction was mixed and the activation energies increased. The products from the thermal reaction were N₂, H₂, CO, HCN, and SiF₄, along with some black solid deposited on the vessel walls. Acetylene was virtually absent. The explosion products were the same as these except that acetylene was also found. More moles of product were formed per mole of 1,2-DP for explosive decomposition than for nonexplosive decomposition. The gaseous products from explosion consisted of approximately 75% nitrogen and 25% acetylene. The yield of HCN was unexpectedly low. Explosion of 1,2-DP does not involve initial dissociation into propylene and N₂F₄, since a 1:1 mixture of these compounds required a higher pressure to explode than 1,2-DP at a given temperature. The explosion limit data for 1,2-DP were shown to be inconsistent with the concept of a pure thermal explosion or a branched-chain explosion with chain breaking occurring only at the vessel walls. The explosions were interpreted as being partly thermal and partly branched-chain, with chain breaking occurring both at the surface and in the gas phase. The chemical and kinetic evidence suggested a mechanism of the form:



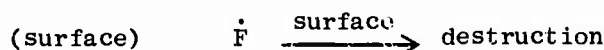
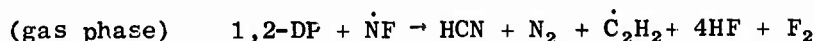
There is probably more than one type of chain carrier, $\dot{X}$. The following reactions were suggested from the observed products:

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and



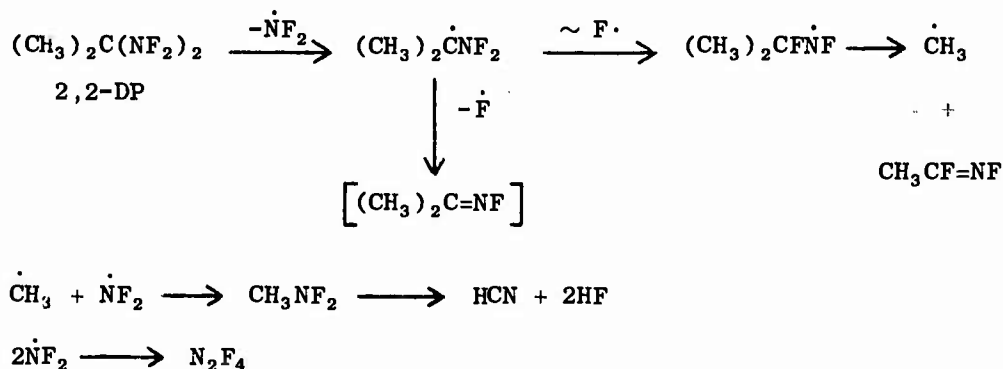
The $\dot{\text{C}}_2\text{H}$ radical is relatively stable and unreactive.

ARC^{48-51, 262, 264} also studied the gas-phase thermal decomposition and explosion of 2,2-DP, 2,2-bis(N,N-difluoroamino)propane, in the static pyrex reactor. At pressures of 25 to 73 mm Hg and temperatures of 248-275°C, the thermal decomposition was homogeneous and first-order in 2,2-DP. The decomposition kinetics were similar to those of 1,2-DP. Again, total decomposition products were observed: HCN, SiF₄, N₂, and H₂, along with black solid on the vessel walls. Very little acetylene was found. The explosion limit of 2,2-DP was examined between 292-334°C and 5 to 40 mm Hg. 2,2-DP was considerably more unstable than 1,2-DP, exploding at temperatures 100°C lower. The products from the explosive decomposition were the same as those from the nonexplosive decomposition, except that acetylene was again present. More product per mole 2,2-DP was formed in the former decomposition than in the latter. Explosion was again interpreted as being partially thermal and partially branched-chain, as described above for 1,2-DP. A chain sequence was also suspected because the low activation energy derived from explosion limit data ($E_a = 41.5 \text{ kcal mole}^{-1}$) was considerably less than the bond energy of a nitrogen-fluorine or carbon-nitrogen bond. In addition, the presence of NO inhibited the decomposition of 2,2-DP and increased the activation energy (65 kcal/mole).

The decomposition of 2,2-DP was studied by SRI^{219, 220, 224, 258} using the flow reactor with fused silica reaction chamber (25-1000°, 10⁻³ mm Hg). Again, 2,2-DP was found to be considerably less stable than 1,2-DP; 2,2-DP

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was half-decomposed at 550-575°C. The identified products were $\text{CH}_3\text{CF}=\text{NF}$ (syn and anti), HCN , CH_3NF_2 , N_2F_4 , and possibly $(\text{CH}_3)_2\text{C}=\text{NF}$. Unimolecular carbon-nitrogen bond homolysis was the rate-limiting, initial step. The mechanism is outlined by:



The 2,2-DP decomposition has also been studied briefly at Rohm and Haas²⁵⁷ in a monel stirred-flow reactor using helium as the carrier gas at a total pressure of one atmosphere and a partial pressure of 2,2-DP of less than one mm. The reaction was examined over the temperature range of 400 to 670°C. Allene was formed in 25 to 50% yield; no HNF₂ was present. Although the reaction was not surface catalyzed, the energy of activation was unusually low (~12 kcal mole⁻¹). A chain reaction and/or a multicenter elimination was the suspected mechanism of decomposition.

The 1,2-bis(N,N-difluoroamino)-2-methylpropane (IBA) decomposition was studied primarily by ARC and SRI. Both studies were under the same respective conditions described above for 1,2-DP and 2,2-DP. In the low pressure pyrolysis, SRI found IBA to be of intermediate stability between 2,2-DP and 1,2-DP; IBA was half-decomposed at 650°C.²²⁰ As for the other NF compounds studied at this laboratory under these conditions, unimolecular carbon-nitrogen bond homolysis again was proposed as the initial rate-determining step in the decomposition.

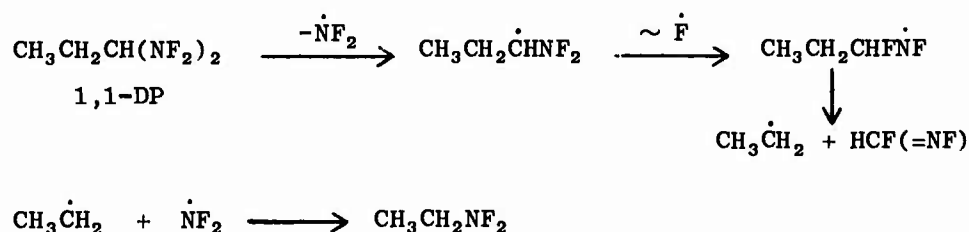
Contrary to these results, ARC^{49,50,261} found JBA to be slightly more stable than 1,2-DP since it exploded at temperatures 15-30°C higher; however, larger vessels than usual were necessary to obtain explosion. At pressures of 5 to 30 mm Hg and temperatures of 400-445°C, the explosion

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products, HCN, C₂H₂, SiF₄, N₂, and H₂, were the same as those obtained from 1,2-DP and 2,2-DP. The products from the nonexplosive decomposition of IBA were also similar to those from 1,2-DP and 2,2-DP (HCN, SiF₄, N₂, H₂). IBA did differ from both 1,2-DP and 2,2-DP in its pressure versus time curve during the preexplosion period. The latter two compounds exhibited slow, smooth increases indicating small amounts of decomposition. IBA, however, showed a moderate but sharp jump during this induction period. This behavior has not been explained, but it may reflect the different order in relative stability for 2,2-DP, 1,2-DP, and IBA found by SRI and ARC.

ARC²⁸⁷ has recently initiated studies on 1,3-bis(N,N-difluoroamino)propane, 1,3-DP. Only the explosion limit has been investigated so far in the static reactor at pressures of approximately 5-7 g mm. Preliminary data indicate that the explosion limit curves for 1,3-DP and 1,2-DP coincide.

Preliminary results found by SRI^{258 266} in the low pressure pyrolysis (10⁻³ mm Hg) of 1,1-bis(N,N-difluoroamino)propane, 1,1-DP, indicate that this compound also decomposes by carbon-nitrogen bond homolysis. 1,1-DP was half decomposed at 650°C. The products identified were HCF=NF (syn and anti) and CH₃CH₂NF₂. There were also indications of considerable amounts of dehydrofluorination. The proposed decomposition scheme was:



The explosion limit data of ARC are not in agreement with the thermal decomposition data of SRI. ARC has found the relative order for decreasing sensitivity to explosion to be 2,2-DP >> 1,2-DP ≈ 1,3-DP > IBA. This

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is in agreement with the relative impact sensitivities of these compounds as determined by ARC. The observed higher rate of thermal decomposition prior to explosion might be a major factor in explaining the lower explosion limit curve of 2,2-DP compared to 1,2-DP. SRI has found the relative order for decreasing sensitivity to thermal decomposition to be $2,2\text{-DP} > \text{IBA} \approx 1,1\text{-DP} > 1,2\text{-DP}$.

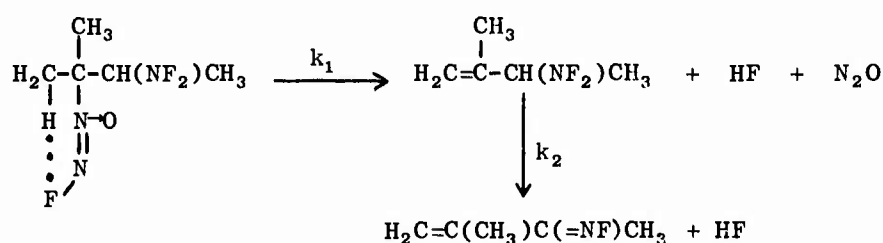
The products found by these two laboratories for thermal decomposition also differ for each compound. While SRI was observing the first products formed in the decomposition, ARC was seeing the final products. Complete decomposition of the initial products found by SRI could possibly yield the final products obtained by ARC; however, this point has not been investigated. In any case, the temperature and pressure conditions were quite different for both sets of experiments. In the SRI work, essentially no gas-gas collisions occurred, while in the ARC work a considerable number of such collisions took place. In view of the different experimental conditions, different relative stabilities, and different products found by these two laboratories, it may well be that two entirely different processes were being observed. However, surface reactions are always suspect.

d. Fluoroazoxy difluoroamino compounds. The mechanism of decomposition of an NF compound clearly depends on what functional groups are present in the molecule in addition to the NF_2 moiety. Fluoroazoxy difluoroamines often appear as impurities in bis-difluoroamines.²⁴² They are also much less thermally stable than the corresponding bis-difluoroamines, thus posing a serious threat to the stability of this latter class of propellant ingredients. The kinetics of thermal decomposition have been studied extensively for only one fluoroazoxy difluoroamino compound.^{194,242} Fluoroazoxy compounds generally yield major quantities of N_2O on thermal decomposition.¹⁹⁴ In an aluminum static reactor at temperatures between 115-145°C, 2-methyl-2-fluoroazoxy-3-(N,N-difluoroamino)-butane, $\text{FN}=\text{N}(\text{-O})\text{C}(\text{CH}_3)_2\text{CH}(\text{NF}_2)\text{CH}_3$, produced N_2O , $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{=NF})\text{CH}_3$,

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and minor amounts of $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}(\text{NF}_2)\text{CH}_3$. The gas-phase kinetics were first-order and the rate of disappearance of starting material was equal to the rate of appearance of products. The low enthalpy of activation, $\Delta H^\ddagger = 33.6 \text{ kcal mole}^{-1}$, and the negative entropy of activation, $\Delta S^\ddagger = -7.2 \text{ e.u.}$,¹⁹⁴ suggested a cyclic elimination mechanism:

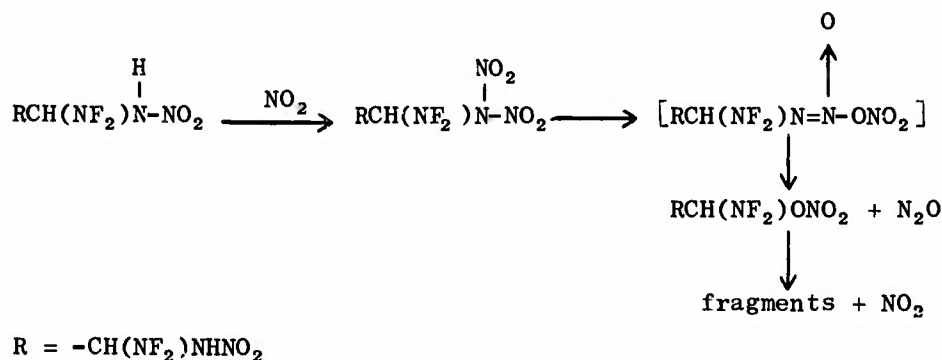


Rate constant k_2 is then considerably larger than k_1 and this latter step may or may not be a surface-dependent dehydrofluorination. The first step, however, appeared to be homogeneous.

e. N-Fluoro nitramines. Thermal decomposition of nitramines ($-\text{N}-\text{NO}_2$) generally results in production of large quantities of nitrous oxide, N_2O . The decomposition of two N-fluoronitramines,¹⁵³ $(\text{CH}_3)_3\text{CNFNO}_2$, and $(\text{CH}_3)_2\text{CHCH}_2\text{NFNO}_2$, exhibited first-order kinetics in organic solvents at low temperatures ($\sim 55-85^\circ\text{C}$). In addition to nitrous oxide, the former compound also produced isobutylene.

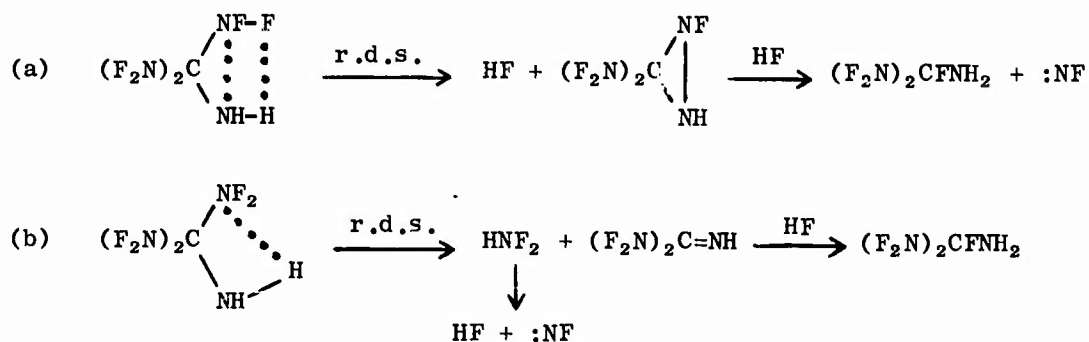
Esso⁹⁸ has done considerable work on the decomposition of a solid difluoroaminonitramine, $[\text{O}_2\text{NNHCH}(\text{NF}_2)-]_2$, BEDNA. At 60°C , the reaction was initially slow. In a closed system, visible quantities of NO_2 were generated and autocatalysis, due to reactions with evolved gases, resulted in explosion. The gaseous products from the thermal decomposition were mainly N_2O and N_2 , plus CO , H_2O , NO , NO_2 , SiF_4 , and N_2F_4 . A reaction sequence was suggested for reaction of the evolved gas, NO_2 , with the solid nitramine:

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Presumably NO also reacts in a similar way with solid BEDNA.

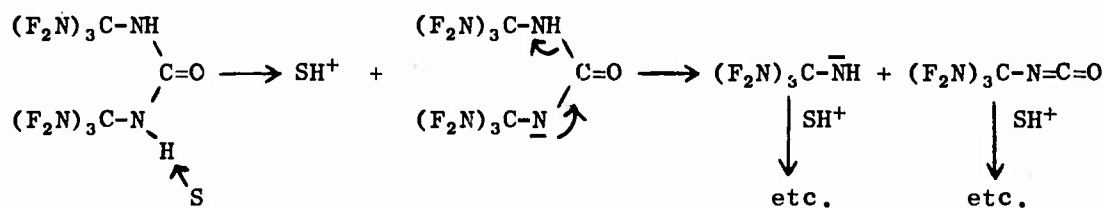
f. Tris(N,N-difluoroamino)methyl group on nitrogen. The lowest member of this series, $(\text{F}_2\text{N})_3\text{CNH}_2$ (Tris-A), was studied by American Cyanamid^{43,264} using a static, passivated monel reactor. Although the gas-phase decomposition was heterogeneous between 150-170°C, the homogeneous conditions were attained by using vessels of low surface-to-volume ratio at temperatures of 185-205°C. The homogeneous rate was first-order in Tris-A and the products were $(\text{F}_2\text{N})_2\text{CFNH}_2$ (Bis-A), $\text{F}_2\text{C=NF}$ (IFM), N_2F_4 , CF_4 , and N_2 . The activation parameters ($E_a = 29.6 \text{ kcal mole}^{-1}$, $A = 10^{11.7} \text{ sec}^{-1}$, $\Delta S^\ddagger = -5.92 \text{ e.u.}$) were low and not in accord with a simple bond homolysis. A cyclic transition state for elimination of HF or HNF_2 was suggested:



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The decomposition of solid Tris-U, $(F_2N)_3CNHC(=O)NH_2$, was examined by the Naval Ordnance Test Station (NOTS)²⁶⁴ in an inert gas atmosphere (usually 100 mm of nitrogen) between 90-130°C. The products were identified as N_2 , CO_2 , N_2O , N_2F_4 , SiF_4 , $RCONH_2$, and by higher molecular weight material and a solid residue. Although the shapes of the pressure versus reaction time curves were not typical of solid phase decompositions, activation parameters were calculated from portions of these curves: $E_a = 30 \text{ kcal mole}^{-1}$ and $A = 2 \times 10^{13} \text{ sec}^{-1}$. The decomposition rates showed only minor sensitivity to the nature of the gas above the solid.

The decomposition of BTU, $(F_2N)_3CNHCONHC(NF_2)_3$, has been studied both in solution and in the solid phase. American Cyanamid Company^{40,260} reported the decomposition of BTU in inert halocarbon (HC-411) solvent in the presence of a few percent diglyme (diethylene glycol dimethyl ether) in the temperature range 100-150°C. Products from this have not been reported. Run in Teflon-coated glassware the reactions followed first-order kinetics. The activation parameters, $E_a = 21.7$ kcal mole⁻¹, $A = 9.3 \times 10^7$ sec⁻¹, $\Delta S^\ddagger = -22.7$ or -24.7 e.u.,⁴⁰ were not typical of a radical process, indicating a possible ionic mechanism. Rate enhancement in solvents of higher dielectric constant was also suggestive of an ionic process and the following scheme was proposed:



S = solvent

This laboratory^{41,42} also reported the solid phase decomposition of BTU at 120°C in a Teflon cup in an inert gas atmosphere (N₂ or He). The solid phase reaction was also unimolecular.

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The work by NOTS^{264,265} on the solid phase decomposition of BTU has been more complete. This reaction was also studied in the presence of nitrogen (200 mm) in the temperature range 130-150°C. The products included N₂, CO₂, N₂O, N₂F₄, RCONH₂, SiF₄, and a solid residue. The activation parameters were only slightly different from those in solution reported above: $E_a = 24 \text{ kcal mole}^{-1}$ and $A = 10^9 \text{ sec}^{-1}$.

g. Tris(N,N-difluoroamino)methyl group on oxygen. Kinetic studies on the gaseous decomposition of methyl tris(N,N-difluoroamino)methyl ether, Tris-E, were recently initiated at American Cyanamid.²⁶⁴ In passivated monel reaction tubes at approximately 150-200°C, the decomposition was homogeneous and followed first-order kinetics. The activation parameters were $E_a \cong 30 \text{ kcal mole}^{-1}$ and $A \cong 10^{11} \text{ sec}^{-1}$. The reaction products have not yet been identified.

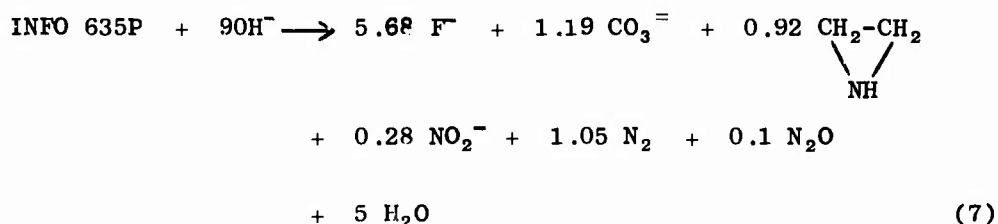
The decomposition of solid Poly FA-BDE $[(F_2N)_3COCH_2\overset{\overset{O}{\parallel}}{C}HCH_2OC(NF_2)_3]$ is quite complex. Dow^{64,264} has studied the slow thermal decomposition of this compound in a static monel reactor at 160-175°C.^{63,64,264} Both continuous vacuum and low pressure conditions were used. The major gaseous products in order of decreasing quantity were $N_2 > NF_3 > COF_2 > CF_4 > HF$; the minor products were N₂O, CO₂, C₂F₆, and N₂F₄. The residue was a carbon-fluorine type of polymer whose composition varied with the different pressure conditions. Hot-stage microscopy indicated a two-stage decomposition of the solid. The first stage might involve carbon-nitrogen bond homolysis to produce $\cdot NF_2$ radicals. Maxima and minima in product formation, determined by mass thermal analysis (MTA), suggested that a major and a minor reaction sequence were operative in this first stage of decomposition. The second stage apparently involves secondary reactions with the residue.

Considerable work has been done on the decomposition of INFO 635P, $(F_2N)_3COCH_2CH_2NH_3^+ClO_4^-$, under various reaction conditions. Dow has examined the decomposition in both basic and acidic solution. Since it is indicated that in the acidic, basic, and solid decompositions of INFO 635P the methoxy carbon appears as CO₂ (or CO₃=) and two of the NF₂

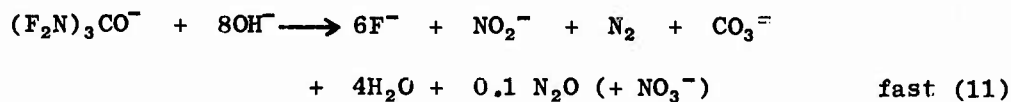
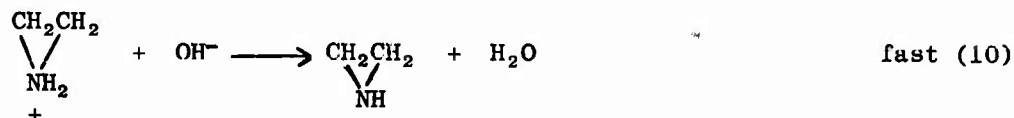
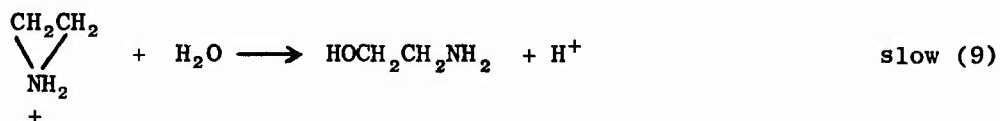
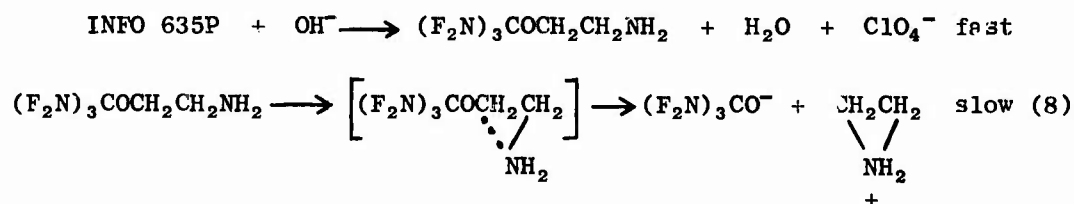
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groups appear as N_2 , the solution studies of Dow have been included in this review. The work in basic solution was run in closed, volumetric flasks, both in an air atmosphere and under vacuum.^{61,62} Most of this work was done in aqueous hydroxide solution at room temperature. The kinetics were first-order in INFO 635P and the products and stoichiometry⁶² of the reaction are represented by:

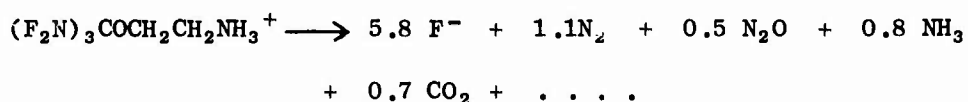


Very little $\text{CH}_2=\text{CH}_2$, C_2H_2 , and N_2F_2 were found. In basic solution, the free amine was present and much more reactive than the salt. The decomposition of the free amine itself was independent of the base concentration. The mechanism for the reaction in base was proposed to involve intramolecular displacement of the methoxy group in the free amine:

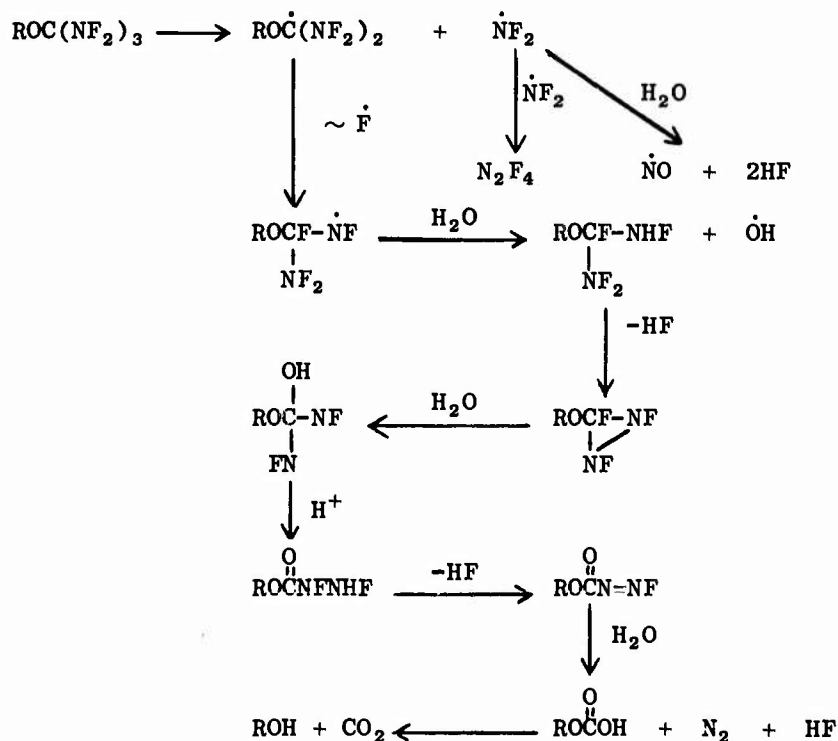


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The kinetic studies of INFO 635P in acidic solution were run in a Teflon-lined, stainless steel, static reactor.⁶² Dilute aqueous perchloric acid solutions (0.1 N) were used in the temperature range of 90-110°C. In weak acidic solution, some free amine was present and its mode of decomposition presumably was similar to that outlined in Eqs. 8 through 11. Decomposition of the protonated amine was represented by the incomplete equation:

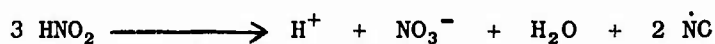
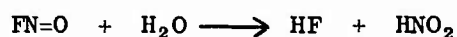


In addition, some N_2F_4 was found, and its yield grew with increasing concentrations of INFO 635P. The reaction was not autocatalytic and no induction period was observed. Initial decomposition was postulated to occur at the tris(N,N-difluoroamino)methoxy function, involving carbon-nitrogen bond homolysis:

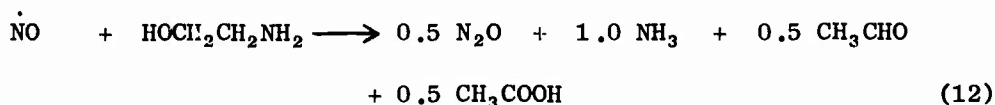


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The cyclic mechanism was invoked to account for the nitrogen formation. The N_2O must then come from reduction of N_2F_4 , $\dot{\text{N}}\text{F}_2$, or $\dot{\text{N}}\text{O}$ and the following possible reaction sequence was suggested:



and



Equation 12 would also account for the presence of ammonia. The other organic products, acetaldehyde and acetic acid, have not yet been identified.

The slow thermal decomposition of solid INFO 635P was also studied by Dow^{63,64,264} in a static system, both in vacuo and in the presence of product gases in the range 160-175°C. In the earlier work with a monel reactor, there was evidence that the solid was reacting with the reactor and all later work was done in platinum. The gaseous products formed in a platinum reactor in the presence of accumulated product gases, in decreasing order of abundance, were $\text{CO}_2 > \text{N}_2 > \text{N}_2\text{O} > \text{CO} > \text{SiF}_4 > \text{ClCN} > \text{N}_2\text{F}_4 > \text{NO} > \text{HCN} \sim \text{CF}_4$.²⁶⁴ The residue consisted of ammonium perchlorate plus an amorphous material. The products formed in vacuo were slightly different from these. It was concluded that secondary gas-gas and gas-solid reactions were significant and masked the primary solid decomposition. Induction and delay periods in the pressure versus time curves suggested a multistage decomposition for solid INFO 635P. Both hot stage microscopy and mass thermal analysis indicated a two-stage decomposition. It was not clear, however, if decomposition of solid INFO 635P involved initial

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carbon-nitrogen bond homolysis to produce $\cdot\text{NF}_2$ radicals or nitrogen-hydrogen bond cleavage to produce the free amine and perchloric acid.

Preliminary work on the decomposition of solid INFO 635P has been reported by Lockheed.²⁶⁴ The temperature of a ribbon coated with INFO 635P was suddenly increased and the thermal decomposition of the coating was followed by mass spectrometry. The products identified thus far include $\text{CH}_2\text{-CH}_2$, CO_2 , and N_2O .
 NH

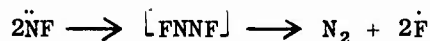
The results obtained by NOTS^{260,264,265} on the thermal decomposition of solid INFO 635P are in agreement with those of Dow. At this laboratory, the decomposition was studied in a static glass reactor in which the gaseous products were allowed to accumulate in a vacuum. Between 140-215°C, the product gases were N_2 , CO , CO_2 , NO , N_2O , N_2F_4 , and SiF_4 and the residue consisted of ammonium perchlorate and some organic material. The effect of added gases and the dependency of the reaction on the total pressure were examined. Reproducibility was not particularly good and there was variation in the activation parameters with the sample used.

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4. Summary

Difluoroamino compounds generally decompose by initial unimolecular bond homolysis under homogeneous reaction conditions. The mechanism for thermal decomposition most frequently encountered is cleavage of a carbon-nitrogen bond to produce $\dot{\text{N}}\text{F}_2$ radicals. This reaction mechanism has been fairly well substantiated for the decomposition of compounds H,R,T, $(\text{CH}_3)_3\text{CNF}_2$ (SRI), 1,2-DP, 1,1-DP, 2,2-DP, IBA, solid Poly FA-BDE, and acidic INFO 635P. The presence of N_2F_4 ($2\dot{\text{N}}\text{F}_2 \longrightarrow \text{N}_2\text{F}_4$) indicates that $\dot{\text{N}}\text{F}_2$ radicals have been produced sometime during the reaction, but not necessarily in the first step. In addition to the compounds listed above, N_2F_4 has been detected among the decomposition products of solid BTU, solid Tris-U, Tris-A, solid BEDNA, solid INFO 635P, and PFG. Nitrogen trifluoride indicates that both $\dot{\text{N}}\text{F}_2$ and $\dot{\text{F}}$ radicals are present during the decomposition ($\dot{\text{N}}\text{F}_2 + \dot{\text{F}} \longrightarrow \text{NF}_3$). This product was found for H,R,T,PFG, 1,2-DP, and solid Poly FA-BDE (N_2F_4 was also found for all these compounds). The $\dot{\text{F}}$ radicals may have been formed directly in the decomposition or indirectly by a reaction such as



Nitrogen-fluorine bond homolysis has been proposed for the first step in the decomposition of the imine, PFF. By analogy, PFG might also decompose by a similar mechanism. Although N_2F_4 and NF_3 are produced, decomposition of the imine, PFG, apparently does not involve initial carbon-nitrogen bond homolysis.

Additional mechanisms have been invoked to account for the first-order kinetics, activation parameters, and/or products for the other compounds reviewed. These mechanisms either partly or exclusively involve functional groups other than the NF_2 - moiety (Tris-A, basic INFO 635, BTU in solution, and the fluoroazoxy difluoroamine).

The most significant mechanistic information has been gained for the gaseous decompositions of the simpler difluoroaminoalkanes, both perfluoro and hydrogen-containing compounds. Information has been

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obtained, particularly for these compounds, regarding not only the initial steps, but also subsequent steps in the thermal decomposition. The carbon radicals produced by initial carbon-nitrogen bond homolysis in R, H, and T readily lose fluorine atoms to give the corresponding N-fluoroimines. This may also be true for 2,2-DP. The analogous carbon radicals for 1,2-DP can lose an additional $\dot{\text{N}}\text{F}_2$ to yield propene, the reverse of the olefin- N_2F_4 addition reaction. Another important reaction involving these carbon radicals has been observed for several compounds. This is intramolecular 1,2 or 1,3 migration of a fluorine atom from the NF_2 -group to the carbon radical. Such a migration has been well substantiated in the decomposition of H, 1,2-DP, 1,1-DP, and 2,2-DP, and it has been proposed for PFF (Eq. 6 is energetically more favorable than Eq. 5) and acidic INFO 635P. By analogy, it may also be operative in the decomposition of R, T, PFG, and solid INFO 635P. Fluorine migration from nitrogen to carbon is an exothermic reaction which could prove to be an important process in an explosion. If the initial rate-limiting step, or subsequent step, in a thermal decomposition leading to an explosion is a unimolecular bond homolysis, or intramolecular migration, little can be done to inhibit the reaction and stabilize the compound. However, certain additives might be effective in trapping the initial products, preventing possible chain reactions leading to explosion.

There is some question whether the decomposition of difluoroamino compounds is a radical chain process. ARC has described the explosions of 1,2-DP, 2,2-DP, and IBA as being partly thermal and partly branched-chain with $\dot{\text{F}}$ and $\dot{\text{N}}\text{F}_2$ as chain carriers. The exact process for thermal decomposition is ambiguous. Dow has suggested that decomposition of Compound T might involve a chain reaction of the initially formed $\dot{\text{N}}\text{F}_2$ radicals with T. On the other hand, Rocketdyne has proposed that the decompositions of R and T involve nonchain radical mechanisms. The possibility of a chain mechanism for decomposition has not been thoroughly investigated.

Less useful information is available for the larger polyfunctional difluoroamines. These compounds are usually solids, for which decomposition data tend to be somewhat erratic. This behavior is often attributed

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to trace impurities, nonuniform crystal parameters, or particle size, and the situation is often difficult to improve or correct. In addition, the kinetics are difficult to measure and little can be said about the mechanisms of solid phase reactions. The primary decompositions are often masked by secondary reactions of the product gases with the solid phase (Poly FA-BDE, BEDNA, and INFO 635P). In general, information for the solid phase consists of final products resulting from thermal decomposition and of activation energies determined from autoignition tests. Some solids have been decomposed in solvents and, in certain cases, the reactions in the two phases could be similar (BTU and INFO 635P)

Much of the reported work on the thermal decompositions of difluoro-amino compounds has been complicated by heterogeneous surface catalysis. Vessels made of stainless steel, aluminum, pyrex, and sometimes monel have been found to catalyze decomposition. Since these catalyzed reactions occur at lower temperatures than the homogeneous decompositions, they are of some importance with regard to the storage of these propellant ingredients. Conditions favoring homogeneous thermal decomposition include: (a) high temperatures; (b) large reaction vessels of low surface to volume ratio; and (c) passivated monel, platinum, or Teflon-coated reaction vessels.

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IV COMPILATION OF RAW DATA

The data reproduced in this section are arranged according to empirical formula of the compound, with inorganic preceding organic compounds. The inorganic compounds are arranged according to the alphabetical order of the atoms involved and the carbon compounds according to number of carbons followed by the order H, F, N, O and P. The listing of the test results is generally in order of impact, shock, static, friction and thermal sensitivity tests. The acronym index is useful as a second method for finding sensitivity information on a particular compound. Compound acronyms are given in alphabetical order which lists the compound number after the acronym. The physical state is given at room temperature. The numbers in parentheses following the data statements are report reference numbers listed in the Appendices.

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1. AsF_9N_2

$\text{N}_2\text{F}_3\text{AsF}_6$
(solid)

Decomp slowly to NOAsF_6 in glass. (235)

2. ClFH_3NO_4

$\text{FNH}_3 \cdot \text{ClO}_4$
(solid)

Code: SAP

Impact: Not sens below 40-45 cm; bare anvil; 2 kg wt. (14)

Static Sens: 5 joules at 50% point in argon atmosphere; RDX = 8 joules. (17)

Thermal Stability:

Stable for sev wks at sub-zero temp. (15)

Stable in nickel container at ambient temp for 3 months.

Decomp in monel. Unsatisfactory in stainless steel and Teflon. Tests summarized in table. (17)

Stable for 1 month at -20° in glass. (16)

Decomp in 1 month in Teflon. (16)

Much decomp and etching in 320 stainless steel. (16)

DTA: Exo at 105° ; small exo at 250 and 300. (15)

3. ClF_3N_2

ClNFNF_2
(gas)

Thermal Stability:

Decomp completely after sev hrs at ambient temp. (4)

4. ClNF_2

NF_2Cl
(gas)

Thermal Stability:

No decomp after 2 wks at ambient temp and 270 mm. (176)

No decomp in Pyrex at 100 mm for 18 hrs at 75° plus 4 hrs at 100° . (174)

Some decomp in 16 hrs at 130° . (174)

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5. Cl_2FN

Cl_2NF
(gas)

Thermal Stability:

2.67 mmoles gas/3.06 mmoles GLC pure material at 0° . (4)

6. $\text{FH}_4\text{NO}_4\text{S}$

FNH_3HSO_4
(solid)

Material was relatively inert to impact, friction, and static charge. (9)

Thermal Stability:

Stable at ambient temp for sev days in anhydrous state. (9)

Decomp rapid at 90° . (9)

7. F_2HN

HNF_2
(gas)

Very explosive: Alone and with N_2F_4 and $\text{C}(\text{NF}_2)_4$; table of explosivity. (226)

Thermal Stability:

Stability in glass, stainless steel, and Teflon apparatuses; tables. (229)

Stability in pyrex at ambient temp and 160°F . (18)

No decomp occurred over a 35-day period. (19)

Compound is stable up to 75° and is stable for 24 hrs at 160°F . (19)

Unstable in stainless steel; stability improved by storing in Teflon-coated stainless steel. (227)

Adiabatic compression at -79° and -30°F , table. (19)

Decomposition kinetics. (226)

Thermal stability, table. (226)

Several detonations occurred while working with HNF_2 . (238)

8. F_3N

NF_3
(gas)

Decomposition, flash photolysis. (244)

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9. F_3NO

NF_3O
(gas)

Impact: On various sized samples, table. (138)

Shock Sens: No detonation at 33, 8, and 5 cards. (234)

Thermal Stability:

Graph of pressure vs temp. (229)

NF_3O was not effective in desensitizing Compound R. (229)

10. F_4N_2

N_2F_4
(gas)

Schlagen Impact: Greater than 1334 kg cm, no glass; 330 kg cm with glass; -70° . (151)

Impact: On various sized samples, table. (138)

Sev detonations occurred while working. (238)

Shock Sens: No detonation in 0.025 in diaphragm fixtures; 12 cards. (234)
Not sensitive: (229)

Adiabatic Compression: Not sensitive. (22)

Thermal Stability:

Thermally stable at elevated temps in stainless steel. (229)

Kinetics of free radical decomp. Rate constant, $k \approx 4 \times 10^{13}$ cc/mole-sec in the vicinity of 2500° . (244)

Flash Photolysis. (244)

Kinetics of dissociation. (172) (59)

11. $F_{10}NSb$

NF_4SbF_6
(solid)

Exposure to vibration scraping, and mild impact gave no incident. (203)

Stable to 300° and relatively insensitive to shock. (203)

12. $CBrF_4N$

$BrCF_2NF_2$
(liquid)

Decomposes in light. (134)

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13. CBrF_6N_3

Code: Tris Br

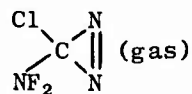
$(\text{F}_2\text{N})_3\text{CBr}$
(liquid)

Impact: 515 kg cm, minimum fire level for 5 kg wt. (68)

Thermal Stability:

Three explosions during prep.

14. CClF_2N_3



Impact: Highly sens. Avoid condensation in beaded traps. (145)

15. CClF_3N_2

$\text{FN}=\text{C}(\text{Cl})\text{NF}_2$
(gas)

Thermal decomposition. (134)

16. CClF_6N_3

Code: Tris Cl

$(\text{F}_2\text{N})_3\text{CCl}$
(liquid)

Thermal Stability:

Stable as vapor in Pyrex. (35)

Three explosions during prep. (69)

17. CF_2N_2

Code: DFC

$\text{F}_2\text{NC}\equiv\text{N}$
(gas)

Thermal Stability:

Very little change; 17 atm/Pyrex capillary/120°/16 hrs. (30)
Does not trimerize. (30)

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18. CF_3NO_2

$\text{FCO}(\text{ONF}_2)$
(gas)

Desensitized by BF_3 addition.(159)

Thermal Stability:

Stable to 1 wk in glass. $\text{Decomp} \rightarrow \text{F}_2\text{CO} + \text{FNO}$.(160)

Decomp is autocatalytic--quickly but without explosion. (159)

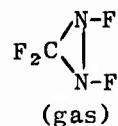
19. CF_3N_3

$\text{F}_2\text{NCF-N}_2$
(gas)

Decomp with light.(30)

20. CF_4N_2

Code: F



Unstable at 25° .(239)

21. CF_4N_2

Code: PFF

FN=CFNF_2
(gas)

Impact: Minimum fire 360 kg cm.(68)

Thermal Stability:

DTA: 208° .(136)

Explosion under uv light in CFCl_3 .(132)

Attempt to polymerize at high pressure ended in explosion.(137)

22. $\text{CF}_4\text{N}_2\text{O}$

CF_3NONF
(gas)

Irradiation with uv light for 1 hr caused decomp .(134)

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23. CF_5N

CF_3NF_2
(gas)

Thermal Stability:

Decomp with light. (133)

Thermally stable to 185° , then defluorination to
 $\text{CF}_2=\text{NF}$ at 350° . (118)

24. CF_5NO_2

$\text{F}_2\text{C}(\text{OF})\text{ONF}_2$
(gas)

Will attack mercury and glass on standing at ambient temp. (161)

25. CF_5N_3

$\text{FC}(\text{NF}_2)\text{C}\begin{smallmatrix} \text{NF} \\ | \\ \text{NF} \end{smallmatrix}$
(gas)

Code: G

Unstable at 25° . (239)

26. CF_5N_3

$\text{FN}=\text{C}(\text{NF}_2)_2$
(gas)

Code: PFG

Impact: 0.1 kg cm at 50% point; modified BuMines. (58)
Less than 0.3 kg cm at 50% point at -78° ; modified
BuMines. (58)
50 cm/3.06 kg wt. (66)
86 cm/3 kg wt; NG = minimum fire level at 100 cm/5 kg wt.
(67)

Schlagen Impact: 150 kg cm with no glass at -70° . (151)

Readily initiated by shock and spark or by liquid-solid or
solid-liquid phase transactions. (58)

Thermal Stability:

DTA: Decomp start at 205° ; sharply increased at 265° . (58)
Exo at 243° . (139)
Exo at 245° yielding CF_4 , N_2 , NF_3 . (21)

Sealed Glass Tube: Gas phase decomp above 110° and etching of
glass surface. (21)

Decomposed at GLC inlet temp of $\sim 200^\circ$. (39)

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26. CF_5N_3 (continued)

Stable for long periods in steel at ambient temp. Good stability over 1 year in "as-received" cylinder. "Pickling" treatment of cylinders omitted. Degreasing treatment continued. (253)

Low temp pyrolysis. (170)

High temp pyrolysis. (170)

Desensitization: Effects of impurities on sensitivity; impurities were isolated. (67)
In fluorocarbon FC-43; table. (142)
By using a few drops of halocarbon oil in traps during vaporization. (72)

Attempt to polymerize with high pressure ended in explosion. (137)

4 out of 49 production runs exploded. (111)

Two explosions in final distillation step. (78)

Two explosions occurred upon transfer of PFG from tank. (206)

Explosion during purification. (238)

Four minor explosions involving material in vapor phase and one fire. (253)

27. CF_6N_2

$\text{F}_2\text{C}(\text{NF}_2)_2$
(gas)

Code: Compound H

Impact: 5.0-6.0 kg cm; 50% point; mod BuMines. (58)

Schlagen Impact: 220 kg cm with no glass; 49 kg cm with glass; -70° . (151)

Thermal Stability:

DTA: Exo at 335° . (136)

Desensitization: Effects of various additives. (166)

Activation energy: 53.6 kcal/mole, gas-phase pyrolysis. (164)(166)

Gas phase thermal decomp; graph; table. (166)

Pyrolysis mechanism. (166)

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28. $\text{CF}_6\text{N}_2\text{O}_2$

$\text{F}_2\text{C}(\text{ONF}_2)_2$
(liquid)

Impact: Failed to detonate at 100 in lb; Compound R = 20 in lb;
ethylnitrate = 5.5 in lb at 50% point; Rocketdyne impact tester.(168)

Thermal Stability:

Will slowly attack mercury. (161)

In Pyrex, has half life of about 2 hrs/0.5 atm at 80°. (161)

In Pyrex, no reaction for 2 hrs at ambient temp. (161)

In s.s., no reaction for 2 hrs/0.5 atm at 84°. (161)

29. CF_6N_6

$(\text{F}_2\text{N})_3\text{C}-\text{N}_3$
(liquid)

Code: Tris Azide
Tris-Az

Impact: 125 kg cm; minimum fire with 5 kg wt. (68)

Thermal Stability:

DTA: Broad endo at 47-59°. (74)

Stable for 1 month as vapor in Pyrex; recovered after
heating at 80° for 3 hours in Pyrex. (39)

Three explosions in preparation. (75)

One explosion when warmed from -196° to ambient temp. (75)

30. CF_7N_3

$\text{FC}(\text{NF}_2)_3$
(gas)

Code: Compound R
R

Impact: 50 kg cm at 50% point; Olin. (135)

In desensitizing solvents and other oxidizers; table.(137)

Varying sample sizes and purity; table.(137)

150 kg cm in polyethylene.(139)

Energy level increased rapidly when N_2O_4 concentration
increases from 40% to 60%. (139)

No explosion at maximum height, 1330 kg cm, with 30%
 N_2F_4 . (139)

65-70 cm; NG greater than 120 cm.(186)

40 kg cm at 50% point; 0°C; mod Olin; 2 premature explosions.(166)

Analytically pure Compound R did not detonate at 127 cm/2 kg wt.
but gave minimum fire level of 125 cm/3 kg wt; minimum
fire level for NG = 100 cm/5 kg wt.(67)

Compound is impact sensitive and may be more so than NG;
3M impact tester.(21)

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30. CF_7N_3 continued

Schlagen Impact: 150 kg cm with no glass; greater than 33 kg cm with glass at 25° . (151)

400 kg cm with no glass; greater than 33 kg cm with glass at -70° . (151)

Shock Velocity: 1609 ± 9 meters per second. (137)

Shock Sens: No stable detonation initiated on gaseous R. (21)

On GC pure samples, tables, graphs; ITTRI shock tube sens tester modified for use at cryogenic temps. (128)

Ignition voltages. (139)

Can be thermally shocked safely over a range of about 350° . (149)

Thermal Stability:

DTA: Exo at 251° , shoulder at 270° and 278° . (135)

Exo maximums at $238-248^\circ$ and $300-332^\circ$; Airco bomb. (24)

Hot Tube: Decomposition products at $250-300^\circ$ in copper or iron. (21)

Sealed Glass Tube: Gas phase decomp above critical temp and etching of glass surface. (21)

Wenograd: Temp to 250 μsec delay, 520. (155)
Graph. (171)

No change after 12 hrs at 200° in CFCl_3 . (132)

Decomp after 12 hrs at 225° in CFCl_3 . (132)

99⁺% pure (3M sample) Compound R decomposes slightly after standing 3 months in glass at 0° . Impurities raised impact sens. (67)

U-Tube compression with N_2F_4 and N_2O_4 , graph. (139)(140)(143)(151)

U-Tube compression with N_2F_4 , graph, table. (150)

Compression Sens: R is readily exploded in modified Aerojet U-Tube tester. (21)

U-Tube compression. (149)(166)(169)

Desensitization: With N_2F_4 and N_2O_4 . (140)(143)(148)(149)

Addition of 30% (weight) of N_2O_4 or N_2F_4 reduces sens to compression. (21)

With heptane or fluorocarbon solvents. (148)

Effect of impurities on sensitivity. Impurities causing increased sens were $(\text{F}_2\text{N})_2\text{CF}_2$ and $\text{F}_2\text{NCF}=\text{NF}$. (67)

Cab-O-Sil does not desensitize R. (228)

No change in monel at $225-250^\circ$ with 25-50% N_2F_4 . (162)

40 mole % N_2F_4 dramatically decreases compression (162)

With dinitromethane and air. (166)

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30. CF_7N_3 (continued)

Thermal decomposition. (131)(140)(143)(151)(163)(164)(242)(244)

Mechanisms of thermal decomposition. (55)(59)(165)(164)

Kinetics and mechanisms of pyrolysis. (55)(166)

Activation Energy: 48.3 kcal/mole, gas-phase pyrolysis. (166)

31. CF_8N_4

$\text{C}(\text{NF}_2)_4$
(liquid)

Code: Compound T
Delta
 Δ
Compound Δ

Impact: 42 kg cm ; 98% pure. (68)
36 kg cm; GC pure. (68)
At various temps; table. (140)

Schlagen Impact: Less than 33 kg cm with no glass at 25°. (151)

Shock Sens: Comparable with Compound R and PFG. (21)
More sensitive than lead azide; ITTRI shock tube
tester modified for use at cryogenic temps. (128)

Thermal Stability:

DTA: Exo start at 210°; exo peak at 250°. (143)
Exo maximum at 240°. (59)

Wenograd: Graph. (171)

Adiabatic compression. (166)

No change after 4 hrs at 70°. (33)(59)

No change after 12 hrs at 125°; 20% solution in CFCl_3 in glass. (59)(139)

Complete decomp in 12 hrs at 165°; 20% solution in CFCl_3
in glass. (59)

Activation Energy = 40.4 kcal/mole, gas-phase pyrolysis. (166)

Desensitization: N_2O_4 exhibits a pronounced desens effect. (33)
 N_2F_4 does not desensitize compound Δ . (229)
Effects of sev additives. (166)

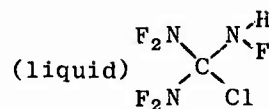
Five explosions - 2 of them were minor vapor phase explosions. (253)

Decomposition kinetics, gas-phase. (39)(42)(59)(60)(61)(62)(165)
(166)(169)(248)

High temp pyrolysis, gas-phase. (166)(171)

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32. CHClF_5N_3



Vapor dissociates within a few min.; yields PFG + HCl in presence of Ni metal. Slower dissociation in Pyrex, stable at -79° . (35)

33. CHFNaO_2

NHFCOONa
(solid)

Thermal Stability:

Aqueous solution relatively stable at low temp. (4)

Spontaneous decomp. at $20-25^\circ$. Decomp. products listed. (4)

34. CHF_4N_2

$\text{HN}=\text{C}(\text{NF}_2)_2$
(liquid)

Code: F_4G

Thermal Stability:

F^{19} nmr: unchanged after sample was kept at ambient temp in Freon 11 for 22 days. (35)

Slight decomp in glass at -78° . (35)

35. CHF_5N_2

$\text{FCH}(\text{NF}_2)_2$
(gas)

Impact: 240 kg cm; 99% pure; 5 kg wt. (68)

36. CHF_5N_2

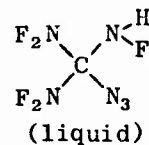
$\text{F}_2\text{NCF}_2\text{NFH}$
(gas)

Code: HH

Stable in vapor phase for sev. wks. Slowly dehydrofluorinates to PFF liquid phase over four month period. (139)

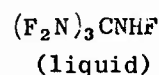
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37. CHF_5N_6



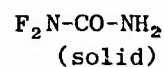
Stable in halocarbon solvents. (35)

38. CHF_7N_4



Stable for 13 wks. at 25° in Freon 11 - $\text{Si}(\text{CH}_3)_4$ solution. (34)

40. $\text{CH}_2\text{F}_2\text{N}_2\text{O}$



Code: DFU

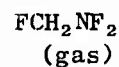
Impact: 30 kg cm. (45)
43, 36, and 45 kg cm. (37)
10-20 cm; $\frac{1}{2}$ kg m.s. hammer. (127)

Thermal Stability:

DTA: Melts at 36° . (37)

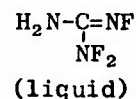
TGA: 87% sublimes up to 125° . (37)

41. $\text{CH}_2\text{F}_3\text{N}$



Impact: 12.0-13.0 kg cm at 50% point; modified BuMines. (58)

42. $\text{CH}_2\text{F}_3\text{N}_3$



Code: TFG

Thermal Stability:

Stable at -25° but decomp. at $0^\circ \rightarrow \text{HNF}_2 + \text{H}_2\text{NC}(=\text{NF})\text{CN}$. (145)

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43. $\text{CH}_2\text{F}_4\text{N}_2$

$\text{CH}_2(\text{NF}_2)_2$
(liquid)

Impact: 0.1 kg cm; 50% point; modified BuMines. (58)

Thermal Stability:

Gas decomp. in Pyrex overnight at $25^\circ \rightarrow \text{HNF}_2$, SiF_4 , a compound with absorbance at 2300 cm^{-1} , and a white solid. (31)

Decomp. after a few hrs in liquid CFCl_3 . (31)

43a. $\text{CH}_2\text{F}_4\text{N}_2$

$\text{F}_2\text{NCF}_2\text{NH}_2$
(gas)

Thermal Stability:

Gas decomposes overnight at 25° yielding HNF_2 , SiF_4 , a white solid, and a compound with absorbance at 2300 cm^{-1} . (31)

Decomp after a few hrs in liquid CFCl_3 . (31)

44. $\text{CH}_2\text{F}_6\text{N}_4$

$(\text{F}_2\text{N})_2\text{C}(\text{NFH})_2$
(liquid)

Code: TH_2

Unchanged in CFCl_3 solution in glass for 18 days at 25° . (145)

45. $\text{CH}_2\text{F}_6\text{N}_4$

$(\text{F}_2\text{N})_3\text{CNH}_2$
(liquid)

Code: Tris A

Thermal Stability:

Thermal gas-phase decomposition; graph. (43)

Stable in Pyrex for 8 days at 50 mm pressure. (32)

46. $\text{CH}_3\text{FN}_2\text{O}$

NHFCNH_2
(solid)

Impact: 34 cm on bare anvil; cm on grit paper; 17 cm on glass-fiber cloth; BuMines type tester at 50% point with 2 kg wt. (12)

Thermal Stability:

DTA: Exo at 128° . (12)

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46. $\text{CH}_3\text{FN}_2\text{O}$ (continued)

Storable at 0° for sev. months. (14)

When stored at ambient temp., compound turns yellow and yields $\text{NH}_2\text{CON}=\text{CONH}_2$. (14)

Aqueous solution storable for sev. wks. at 0° . (14)

Aqueous solution not storable for sev. wks. at ambient temp.; yields $\text{NH}_2\text{CON}=\text{NCONH}_2$. (14)

47. $\text{CH}_3\text{F}_2\text{N}$

CH_3NF_2
(gas)

Impact: 6.0-7.0 kg cm; 50% pt.; modified BuMines. (58)

Thermal gas-phase decomp. (192)

48. $\text{CH}_3\text{F}_2\text{NO}$

$\text{F}_2\text{NCH}_2\text{OH}$
(liquid)

Impact: ~ 10 kg cm. (45)
7-10 kg cm. (225)

49. $\text{CH}_6\text{FNO}_3\text{S}$

$\text{FNH}_3\text{CH}_3\text{SO}_3$
(solid)

Impact: Not sens below 150 cm/2 kg wt. (10)

Static Sens: Pos. at 5 joules, neg. at 2.5 joules. (10)

Thermal Stability:

Stable for sev. weeks at ambient temp. in inert atm. (10)

Decomp. rapid at $105-110^\circ$. (10)

50. $\text{C}_2\text{Cl}_2\text{F}_6\text{N}_4\text{O}$

$(\text{F}_2\text{N})_3\text{CON}=\text{CCl}_2$

Code: OTPO

Impact: Probably sens. (147)

Thermal Stability:

No decomp. in glass at ambient temp. for 3 wks. (147)

51. $\text{C}_2\text{F}_3\text{N}_3$

$\text{FN}=\text{C}(\text{CN})\text{NF}_2$
(liquid)

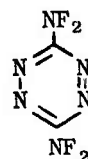
Code: PCF

Five preparation runs exploded. (145)

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52. $C_2F_4N_6$

Unstable. (209)



53. $C_2F_6N_4$

Code: RN

$(F_2N)_3CCN$
(liquid)

DTA: Exo starts at 135° , rapid at 160° . (142)

54. $C_2F_6N_4O$

Code: Tris I

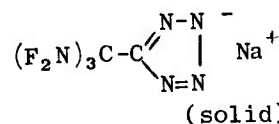
$(NF_2)_3C-N=C=O$
(liquid)

Thermal Stability:

Unchanged for 20 hrs at $125-130^\circ$, then 2 hrs at 150° . (39)

Two explosions during preparation. (69)

55. $C_2F_6N_7Na$



(solid)

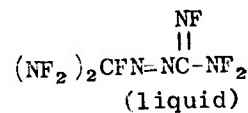
Static sens: Extremely sens.; therefore, handled in solvents. (144)

56. C_2F_7N

$CF_3CF_2NF_2$
(gas)

Gaseous pyrolytic decomp. yields trifluoroacetonitrile at $150-300^\circ$. (118)

57. $C_2F_8N_6$



(liquid)

Code: F₈ADF

Thermal Stability:

Storage of crude product at dry ice temp. for sev. wks.
led to sev. spontaneous explosions. (119)

Storage of pure product under vacuum at -80° for sev. days
led to azide impurity. (119)

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58. $C_2F_{10}N_4$ Code: E $(F_2N)_2CFNFCF_2NF_2$
 $F_{10}CG$ (liquid)

Impact: 20-25 gm cm at 0°. (65)

Thermal Stability:

Stable at 25°. (239)

59. $C_2F_{11}N_5$ Code: $F_{11}BG$ $(F_2N)_2CFNFCF(NF_2)_2$
 (liquid)

Impact: 12 to 14 cm/2 kg wt; NG greater than 120 cm. (86)

20 to 25 g cm at 0°. (65)

Less than 1 kg cm at 70°F; Olin; table. (58)

Thermal Stability:

DTA: Endo at 100-130°; exo at 227-240°; then explosion. (57)

Desensitization: N_2F_4 , Cl_2 , and gelation with nitroso rubber did not desensitize $F_{11}BG$. (57)

Thermal decomp. (57)

60. $C_2F_{12}N_6O_2$ $(NF_2)_3C-O-O-C(NF_2)_3$
 (liquid)

Solution decomposition. (147)

61. $C_2HF_5N_4O$ $(F_2N)_2C \begin{matrix} \nearrow NHF \\ \searrow NCO \end{matrix}$
 (liquid)

Thermal Stability:

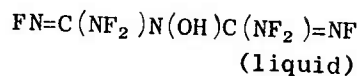
No change in F^{19} nmr for 78 days at ambient temp in Freon 11 solution. (32)

62. $C_2HF_5N_6O_6$ $\begin{matrix} NF_2 \\ | \\ HFN-C-C(NO_2)_3 \\ | \\ NF_2 \end{matrix}$

Unstable, hazardous handling. Two explosions occurred in attempt to isolate. Used in solution. (206)

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63. $C_2HF_6N_5O$

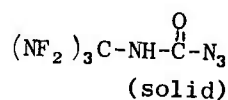


Impact: Much less sens. than PFG. No explosion during sev. months of handling. (245)

Thermal Stability:

No sign of decomp. in glass after 15 hrs at 100°. (245)

64. $C_2HF_6N_7O$



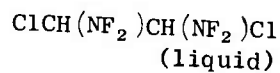
Code: Tris-carbamyl azide

Impact: 5 kg cm/2 kg wt. (39)

Thermal Stability:

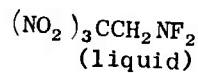
Small amount of decomp. noted on standing in atmosphere.
Stable under N_2 . (39)

65. $C_2H_2Cl_2F_4N_2$



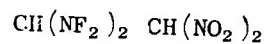
Impact: 18 kg in. (87)

66. $C_2H_2F_2N_4O_6$



Stable; is high boiling liquid. (206)

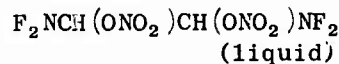
67. $C_2H_2F_4N_4O_4$



Impact: 1 cm/2 kg; RDX = 30 to 35 cm. (5)

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68. $C_2H_2F_4N_4O_6$

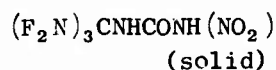


Impact: 1.9 kg in at 50% point; Picatinny. (185)

Thermal Stability:

Compound turned pale blue after 2 hrs, and completely
decomp. overnight. (96)

69. $C_2H_2F_6N_6O_3$



Code: Nitro-Tris U

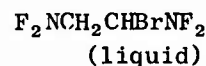
Thermal Stability:

Dry solid stable for 1 day in N_2 atm. (42)

Stable in CH_2Cl_2 for 1 day. After 14 days $\rightarrow$ Tris A. (42)

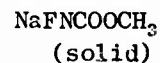
Deliquescent after 5 min; decomp. overnight $\rightarrow$ volatile gases. (42)

70. $C_2H_3BrF_4N_2$



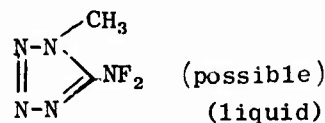
Impact: 12 kg in; RDX = 20 kg in. (88)

71. $C_2H_3FNNaO_2$



Sev. explosions while isolating the dry salt. Probably due to
rapid thermal decomp. above 0° . (156)

72. $C_2H_3F_2N_5$



Neat liquid exploded, destroying fluorination apparatus. (210)

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73. $C_2H_3F_3N_2O$

$FN=C(NF_2)OCH_3$
(liquid)

IR unchanged after 13 wks. at 25° . (139)

74. $C_2H_3F_6N_3$

Code: TDE

$F_2NCH_2CH(NF_2)_2$
(liquid)

Impact: 1 to 1.5 kg in; Picatinny. (96)

Thermal Stability:

GLC purity--60.0% and 80.0%--after two samples were stored at 60° for 120 hrs in stainless steel; 87.0% GLC pure with acid treated stainless steel. (97)

Decomposition studies, liquid-phase. (97)

75. $C_2H_3F_6N_3O$

Code: Tris-E

$CH_3OC(NF_2)_3$
(liquid)

Impact: On various sample sizes; table. (137)

Thermal Stability:

VTS: 75 cc/gm/24 hrs at 60° . (96)

Stable at 25° . (137)

GC pure sample unchanged after 150 hrs in stainless steel at 60° . (97)

Detonation in glass after short time. (97)

In metal, H_2O vapor caused rapid decomp. after more than 24 hrs. (97)

76. $C_2H_3F_6N_5O$

Code: Tris-U

$(NF_2)_3CNHCONH_2$
(solid)

Impact: 26 kg cm with 2 kg wt. (244)

Less than 4 cm; 0% fires; 2 kg wt. (39)

25.5 kg cm. (37)

Thermal Stability:

DTA: Exo at 136° . (100)

Decomp. at $100-110^\circ$. (37)

TGA: Wt. loss at 110° . (37)

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76. $C_2H_3F_6N_5O$ (continued)

VTS: 2.5 cc/gm/20 hrs at 60° . (100)
43 cc, gm/100 hrs at 60° . (100)
3.96 cc/gm; needles--no inclusions. (40)
Taliani: 5.5 cc/gm, $5\frac{1}{2}$ hrs at 70° in N_2 atmosphere. (37)
3.7 cc/gm/150 min at 70° . (37)
Solid showed no change in IR spectrum or color after
 $1\frac{1}{2}$ months at 25° . (39)
DTA, TGA, and Taliani tests results. (244)

77. $C_2H_4ClF_6N_5O_5$

$(F_2N)_3CNHCONH_3 ClO_4$
(solid)

Code: TUP

Impact: 21 kg cm/2 kg wt. (244)
Bottle Drop Test: No explosion occurred when a ~ 10 mg. sample
of TUP in a glass vial was dropped from a
height of 70 cm. (39)

Thermal Stability:

VTS: Trace gas 100 mg 20 hrs at 25° . (36)
Stable in CH_3NO_2 for 6 hrs. (36)
Taliani: 37.0 cc gm $5\frac{1}{2}$ hrs at 70° in N_2 atmosphere. (37)
DTA, TGA, and Taliani tests. (244)

78a. $C_2H_4F_2N_4O_3$

$O_2NNHCONHCH_2NF_2$
(solid)

Impact: 10 cm; $\frac{1}{2}$ m.s. hammer. (121)
Explosion Point: 136° . (121)

78b. $C_2H_4F_2N_4O_4$

$[O_2NNFCH_2-]_2$
(liquid)

Impact: Exploded violently below 1 cm when 2.0 kg wt was used. (5)

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78c. $C_2H_4F_3N_2O$

$CH_3OC(NF_2)NFH$
(liquid)

Thermal Stability:

VTS: 182 cc/gm/24 hrs at 60°. (96)

79. $C_2H_4F_4N_2$

$CH_3C(NF_2)_2H$
(liquid)

Thermal Stability:

VTS: 26 cc/gm/100 hrs at 90°. (93)
3432 cc/mole/100 hrs at 90°. (93)
Graph: Gas evolved vs time. (92)

80. $C_2H_4F_4N_2$

Code: BDE

$F_2NCH_2CH_2NF_2$
(liquid)

Impact: 20 to 30 kg cm. (45)
11 kg in; RDX = 20 kg in. (88)
24 kg cm; 50 % pt; modified BuMines. (58)
Neg. to 140 in lbs/2 lb wt at 3°, N₂ atm. (158)
~ 50 in lb/2 lb wt at 50% point in air. (158)
DuPont Drop Test: Positive at 2 in; 5 kg wt; 50% point. (79)
Ball Drop: Shot at less than 35 in. with 8.3 gm ball. (79)
Static Sens: Shot at ~ 8200 M.E.V. (79)

Thermal Stability:

Hot Bar: Evaporated at 250°. (79)
Desensitization: With additives in hot-wire screen test,
table. (54)

80a. $C_2H_4F_4N_2O_2$

$F_2NCH(OH)CH(OH)NF_2$
(liquid)

Thermal Stability:

VTS: 171 cc/gm/100 hrs at 60°. (93)
28,044 cc/mole/100 hrs at 60°. (93)

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81. $C_2H_4F_4N_4O_2$

$F_2NCH_2CH(NF_2)NHNO_2$
(liquid)

DuPont Drop Test: 11 kg cm at 50% point. (79)

Ball Drop: Neg. at 10 in, detonated at 12 in. with 8.3 gm ball. (79)

Base Load Test: No. 1 lead plate. (79)

Static Sens: Shot at 33,600 M.E.V. (79)

Thermal Stability:

Copper block: Shot at 140°. (79)

Hot bar: Shot at 250°. (79)

VT3: 200 cc/gm/100 hrs at 90°. (93)

38,400 cc/mole/100 hrs at 90°. (93)

Explodes spontaneously on storage. (92)

Triply distilled kept for sev. weeks. (92)

82. $C_2H_4F_4N_4O_2$

$(F_2NCH_2)_2NNO_2$

Code: BDMN

Impact: 10-20 cm; $\frac{1}{2}$ kg m.s. hammer. (127)

Explosion Point: 140°. (127)

Thermal Stability:

VT3: Autocatalytic decomp. at 60°; initial rate:
19.5 cc/gm/100 hrs. (127)

Decomposition autocatalytic. (123)

83. $C_2H_4F_4N_6O_4$

$[O_2NNHCH(NF_2)]_2$
(solid)

Code: BEDNA

Impact: 10-15 kg in. (95)

Thermal Stability:

DTA: Exo at 113-115°. (95)

Mechanism of decomp., thermal, various conditions. (98)

Storage in high vacuum prevents explosion but still decomp.
in 1 to 2 wks. (98)

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83. $C_2H_4F_4N_6O_4$ (continued)

Thermal decomp. autocatalyzed. (98)

Decomp. in closed vessels end in explosion. (98)

Ethanolysis prep. - little or no gas, in vacuum, for 60 days at ambient temp. (97)

Ethanolysis prep. - little or no gas for 16 hrs at 60°. (97)

Hydrolysis prep. evolves gas immediately. (97)

Ethanol has some stabilizing effect. (98)

VTS: Graph of gas evolved vs time. (98)

84. $C_2H_4F_5N_3O$

$CH_3OC(NF_2)_2NHF$
(liquid)

Impact: On various sample sizes; table. (137)

Thermal Stability:

Storage at -78° greatly reduces decomp. (53)

85. $C_2H_5F_2N$

$CH_3CH_2NF_2$
(gas)

VTS: Only few % decomp. after 4 hrs at 270° + 1 hr at 310° at 100 mm. (173)

86. $C_2H_6F_2N_2O_2S$

$H_3CSO_2NHCH_2NF_2$

Impact: Greater than 200 cm; ½ kg m.s. hammer. (127)

87. $C_2H_6F_4N_6O_5$

$O_2NNHCH(NF_2)CH(NF_2)NHNO_2 \cdot H_2O$
(solid)

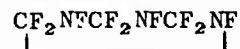
Code: BEDNA · H₂O

DTA: Broad exo start at 83°, deflagration at 101°, peak at 110°. (95)

TGA results. (95)

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88. $C_3F_9N_3$

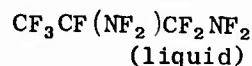


(liquid)

DTA: Slow exo at 413° . (135)

Thermal decomposition, gas-phase. (118)

89. $C_3F_{10}N_2$



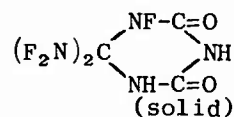
(liquid)

Thermal Stability:

VTs: 0.1 cc/gm/100 hrs at 90° . (94)

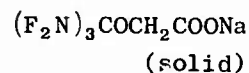
Graph: Gas evolved vs time. (94)

90. $C_3H_2F_5N_5O_2$



Stable at ambient temp. in air. (35)

91. $C_3H_2F_6N_3NaO_3$

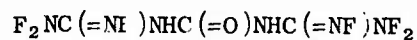


(solid)

Stable in air with normal handling. (141)

An attempt to take m.p. of ~ 2 mg exploded at 115° with sufficient force to leave small indentation on the metal heating stage. (142)

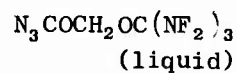
92. $C_7H_2F_6N_6O$



Code: BTGU

Becomes yellow and m.p. drops 5° over 4 day period. (42)

93. $C_3H_2F_6N_6O_2$



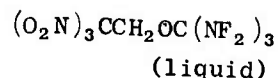
(liquid)

Code: FA-GA

DTA: Exo. at 109° . (102)

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94. $C_3H_2F_6N_6O_7$



Code: FA-TNE

Impact: 7.5 kg cm at 50% pt.; Picatinny. (106)

Friction Screw: Negative with no grit; positive at Hardness 5.5.

Thermal Stability:

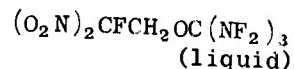
DTA: Explodes at 150°, decomp. after 132°. (99)

Autoignition, 5 sec.: 223°. (106)

VTS: 1.5 to 1.8 cc/g/100 hrs at 60°; off-scale in less than
24 hrs at 90°. (108)

2.4-3.4 cc/gm/6 days at 60° plus 1 day at 90°. (99)

95. $C_3H_2F_7N_5O_5$



Code: FA-FDE

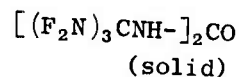
Impact: 9 kg cm at 50% pt.; Picatinny. (106)

Spark: Negative at 0.96 joules. (106)

Friction Screw: Negative at Hardness 5.5, positive at Hardness 6. (106)

Autoignition, 5 sec: 230°. (106)

96. $C_3H_2F_{12}N_8O$



Code: BTU

Impact: 38 kg cm/2 kg wt at 50% point. PETN = 116 kg cm. (42)
Detonated at 1 inch; $\frac{1}{2}$ in. steel ball. (78)
3.9 cm; NOL drop height. (146)
12 kg cm; (284)

Static Sens: Detonated at an average of 0.0150 joule. (78)

Detonated at 0.0262 joule; Negative at 0.023 joule. (40)

Friction Screw: Positive at Hardness 4. (284)

Thermal Stability:

DTA: Decomp start at 97-105°; moderate exo at 140-144°;
exo 170-173°. (77)

Exo start at 145°; peak at 180°; endo at 192°; exo maximum
at 192-225°. (42)

For material isolated and recrystallized in sev ways; table. (78)
Analysis of DTA behavior; graph. (43)

TGA: Weight loss start at 100° in air and N₂; ends at 170°. (42)
Analysis. (38)

Taliani, DTA and GTA results. (244)

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96. $C_3H_2F_{12}N_8O$ (continued)

Taliani: Recrystallized sample - 13.4 cc/gm/6 hrs at 90°. (42)

Sublimed sample - 4.1 cc/gm/6 hrs at 90°. (42)

3.2 cc/gm/150 min at 70° in N_2 atmosphere. (37)

Comparative Taliani test; table, graph. (38)

No decomp after 16 days at 25°. (38)

Stable in Pyrex for 1 month at ambient temp. (42)

Storage stable. (78)

Effect of various solvents on stability; table. (41)

Decomposition kinetics, solid and solution. (40)(41)(42)(248)

Shock Tube Sens: 250 μ sec delay to explosion; 729°K (NG = 750°K) (289)

97. $C_3H_3F_4N_3$

$F_2NCH_2CH(NF_2)CN$
(liquid)

Impact: 9 kg cm. (45)

98. $C_3H_3F_4N_3O$

$F_2NCH_2CH(NF_2)NCO$
(liquid)

Code: DEI

Impact: ~ 10 kg cm. (82)

1 to 4 in./2 kg wt. (79)

Desensitization: Dilution with various solvents; impact sens run on each; acetone, cyclohexanone and "Halocarbon Oil" found to be most effective; table. (79)

99. $C_3H_3F_4N_5O_3$

Code: MNBDI

$F_2NCHNNO_2$
|
 F_2NCHNH
(solid)

Impact: Less than 5 cm; $\frac{1}{2}$ kg m.s. hammer. (125)

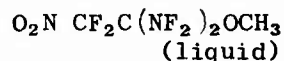
Explosion point: 152° (125)

Thermal Stability:

VTS: 8.0 cc/gm/100 hrs at 60°. (125)

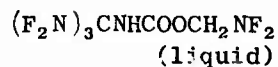
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100. $C_3H_3F_6N_3O_3$



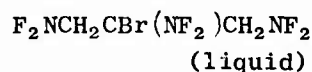
Storage stable at ambient temp. (208)

101. $C_3H_3F_8N_5O_2$



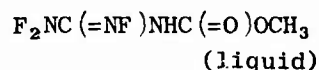
Very shock sensitive. A small sample in a capillary pipette detonated when the pipette was broken. (98)

102. $C_3H_4BrF_6N_3$



Impact: 18 kg in; RDX = 20 kg in. (88)

103. $C_3H_4F_3N_3O_2$

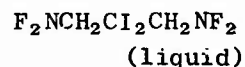


Thermal Stability:

Neat liquid at 25° for 2 months remained colorless and unchanged. (42)

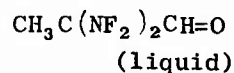
Unchanged in solution in $CFCl_3$ in Pyrex at 25° for 3 months. (42)

104. $C_3H_4F_4I_2N_2$



Decomp. yields I_2 when exposed to air. (92)

105a. $C_3H_4F_4N_2O$



Nonvolatile highly explosive oil. Work on it discontinued. (97)

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105b. $(C_3H_4F_4N_2O)_n$

$[-OCH_2C(NF_2)CH_2NF_2]_n$
(solid)

Code: PBEP

Impact: 15 cm with 2 kg wt. (272)
~ 14-25 kg cm with various samples. (291)
Comparable to HPE, NG, TVCPA. (292)

Friction Screw: Positive at Hardness 5.5. (291)

Static: Negative at 25 joules. (272)

Thermal Stability:

DTA: Exo, 198°. (272)
Exo, 214° and 225°. Varies with production lot, also with aging; table. (291)

VTS: 5.2 cc/gm/240 hrs at 80°. Varies with production lot. (291)

Taliani: 0.5 gm sample/23 hrs at 93° gives 150 mm pressure.
(standard materials, less than 50 mm pressure) (272)

106. $C_3H_4F_4N_2O_2$

$F_2NCH_2CH(NF_2)OOCH$
(liquid)

DuPont Drop Test: 90 kg cm at 50% point. (79)

Base Load Test: No. 5 lead plate. (79)

Static Sens: Shot at 38,400 M.E.V. (79)

Thermal Stability:

Copper Block: Boiled off at 250° (79)

Hot Bar: No reaction at 250°. (79)

107. $C_3H_4F_4N_4O$

$\underline{CONHCH(NF_2)CH(NF_2)NH}$
(solid)

Code: BDI

Impact: 10-20 cm; $\frac{1}{2}$ kg m.s. hammer; NG = 25-30 cm. (243)

Explosion Point: Greater than 300°. (243)

Thermal Stability:

VTS: 0.3 cc/gm/100 hrs at 60°. (127)

Vapor phase explosion. (56)

108. $C_3H_4F_4N_4O_3$

$F_2NCH_2CH(NF_2)N(NO_2)CH=O$
(liquid)

CODE: FDEN

DuPont Drop Test: 2.5 kg cm at 50% point. (84)

Ball Drop Test: Detonated at 10 in. with 8.3 gm ball. (84)

Base Load Test: No. 0 lead plate. (84)

Static Sens: Detonated at 14,680 M.E.V. (84)

Hot Bar: Instantaneous detonation at 250°. (84)

Copper Block: Detonated at 156°, after 4 min 11 sec. (84)

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109. $C_3H_4F_4N_4O_6$

$O_2NOCH_2C(NF_2)_2CH_2ONO_2$
(liquid)

Code: DNBP

Impact: 1-2 kg in; neat. (97)
3 kg in; CH_2Cl_2 soln (3/1). (97)
5 kg in; CH_2Cl_2 soln (6/1). (97)
6 kg in; CH_2Cl_2 soln (12/1); erratic results. (97)
7 kg in; Freon 113 soln (6/1). (97)

Thermal Stability:

DTA: Exo at 186.5° . (95)

No decomp after 100 hrs at 60° . (95)

110. $C_3H_4F_6N_4O_2$

$(F_2N)_3CNHCOOCH_3$
(solid)

Recovered unchanged after 4 hrs heating at $71-6^\circ$ in a sealed tube. (39)

111. $C_3H_4F_6N_4O_2$

$(F_2N)_3COCH_2CONH_2$
(solid)

Code: GA

Impact: 4.0 cm ; NOL drop height. (146)

Shock Tube Sensitivity: 250 μ sec time to explosion at $790^\circ K$
(NG = $750^\circ K$) (289)

112. $C_3H_4F_5N_6O$

$[(F_2N)_2CHNH-]_2C=O$

Did not visibly change on storage for 2 months at ambient temp. (120)

113. $C_3H_5BrF_4N_2$

$F_2NCH_2CH(NF_2)CH_2Br$
(liquid)

Impact: 8 kg in; RDX = 20 kg in. (88)

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114. $C_3H_5ClF_4N_2$

$CH_3C(NF_2)_2CH_2Cl$
(liquid)

Wenograd: Temp to 250 μ sec delay, 438°.(155)

115. $C_3H_5FKNO_2$

$KNFCOOC_2H_5$
(solid)

Impact: Negative at 23 kg cm, positive at 50 kg cm; Olin.(157)

Thermal Stability:

VTS: 65% decomposed after 10 days at ambient temp. (157)

116. $C_3H_5FNNaO_2$

$NaNFCOOC_2H_5$
(solid)

Formation of the sodium salt is used to desensitize
 $HFNCOOC_2H_5$.(6)

Thermal Stability:

Stable in methanolic solvent for sev. wks.(6)

117. $C_3H_5F_2N$

$CH_2=CH-CH_2NF_2$
(liquid)

Impact: 178 kg cm.(45)

118. $C_3H_5F_2NO_2$

$F_2NCH_2OOC=CH_2$
(liquid)

Impact: Greater than 38 kg in; RDX = 9.5 in; Picatinny. (239)

119. $C_3H_5F_4N_3O_2$

$F_2NCH_2CH(NF_2)CH_2NO_2$
(liquid)

Impact: 12.8 kg cm.(45)

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120. $C_3H_5F_4N_3O_3$

$F_2NCH_2CH(NF_2)CH_2ONO_2$
(liquid)

Code: NFPN
BDPN
DPN

Impact: Under various conditions; table. (137)

2.5 kg cm. (79)

2.5 kg cm at 50% point; Olin. (47)

DuPont Drop Test: 2 in/2 kg wt at 50% point. (79)

Ball drop: Negative at 20 in; shot at 22 in with 8.3 gm ball. (79)

Static Sens: Shot at 36,500 M.E.V. (79)

Thermal Stability:

Autoignition temp: Boil off at 250°. (47)

Copper block: Boiled away, at 250°. (79)

Hot Bar: Boil off at 250°. (79)

Desensitization in methylene chloride. (182)

Can be desensitized. (46)

150 and 158 gm batches exploded during stripping. (47)

Exploded when injected into 300°F GLC chamber. (47)

121. $C_3H_5F_4N_5O_3$

$F_2NCH_2N(NO_2)CONHCH_2NF_2$
(solid)

Impact: Less than 5 cm; $\frac{1}{2}$ kg m.s. hammer. (127)

Explosion point: 143°. (127)

122a. $C_3H_5F_6N_3$

$F_2NCH_2CH_2CH(NF_2)_2$
(liquid)

Code: 1,1,3-TDP

12.5 gm exploded as polyethylene cap was removed from its glass container. (257)

122b. $C_3H_5F_6N_3$

$CH_3C(NF_2)_2CH_2NF_2$
(liquid)

Code: 1,2,2-TP

Thermal Stability:

Stable at 60° for 120 hrs. (97)

Decomposition kinetics in aqueous diglyme, 75°. (258)

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123. $C_3H_5F_6N_3$

$F_2NCH_2CH(NF_2)CH_2NF_2$
(liquid)

Impact: 7-18 kg cm.(45)
4-8 kg in; RDX = 20 kg in.(88)

Desensitization: Table of additives.(88)
In dibutyl phthalate.(87)

Thermal Stability:

VTS: 0.9 cc/gm/100 hrs at 90°. (93)
177 cc/mole/100 hrs at 90°. (93)

Graph: Gas evolved vs time. (91)

123a. $C_3H_5F_6N_3O$

$F_2CH_2C(NF_2)_2CH_2OH$
(liquid)

Impact: 2 out of 2 tries fired at 4 in; 2 out of 3 tries fired
at 2.8 in; 1 out of 3 tries fired at 1.9 in.(189)

124. $C_3H_6FNO_2$

$FNHCOOC_2H_5$
(liquid)

No significant decomp observations at ambient temp. Rapid
disintegration in GLC. (156)

125. $C_3H_6F_4N_2$

$CH_3CH_2CH(NF_2)_2$
(liquid)

Code: 1,1-DP

Failure diameter transition high to low velocity waves, about
3.6 mm.(223)

Failure diameter for low velocity wave is less than 1.5 mm.(223)

Thermal Stability:

VTS: 0.4 cc/gm/100 hrs at 60°. (95)
3.9 cc/gm/100 hrs at 90°. (94)

Mixtures with ethanol unstable at 23° and 60°. (94)

Rate of dehydrofluorination: $k \approx 4.00 \times 10^{-3} \text{sec}^{-1}$ in 10%
dioxane- H_2O at 50°. (223)

Dehydrofluorination in aqueous dioxane. (220)

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126. $C_3H_6F_4N_2$

Code: 1,2-DP
1,2-RDP

$CH_3CH(NF_2)CH_2NF_2$
(liquid)

Impact: 35.7 kg cm. (51)
14 kg in; RDX = 20 kg in. (88)

Drop Height: Correlation with peak pressure; Olin. (52)

DuPont Drop Test: Positive at 7 in/5 kg wt; 50% point. (79)

Ball Drop: Negative at 45 in with 8.3 gm ball. (79)

Static Sens: Shot at 25,600 M.E.V. (79)

Explosion limit; graph. (52)

Initiates by shock through .87 cm of Plexiglas. (290)

Width of attenuator at 50% gap: 15.8 $\pm$ 0.6 mm Plexiglas;
nitromethane = 11.1 $\pm$ 0.8 mm. (219)

Failure diameter transition high to low velocity waves; 1.6 mm. (223)

Failure diameter for low velocity wave; less than 0.8 mm. (223)

Thermal Stability:

VTS: 0.1 cc/gm/100 hrs at 90°. (93)
15 cc/mole/100 hrs at 90°. (93)

Gas evolution vs time graph. (92)

Hot Bar: Evaporation at 250°. (79)

Wenograd: Delay time to explosion vs temp; graph, table. (55)

Activation energy for gas-phase pyrolysis = 48 kcal/mole. (50)

Activation energy for low pressure gas-phase pyrolysis =
51 kcal/mole. (220)

Activation energy in high temp range, gas phase = 57.3 kcal/mole.
(165)

Activation energy for thermal decomp in nitrobenzene =
40 kcal/mole. (224)

Activation energy for thermal decomp in gas phase =
51 kcal/mole. (224)

Dehydrofluorination rate, $k = 5 \times 10^{-5} \text{ sec}^{-1}$ in 30% dioxane- H_2O
at 50°. (223)

Decomposition products of very low pressure pyrolysis.
C-N rupture and F migration. (219)(220)(223)(224)

Inhibition of autocatalytic decomp with fluoride salts. (214)

Container effects on decomp. (214)

Products of decomp. (214)

Solvent effects on decomp. (213)(215)

Effect of acid and base on decomp. (217)

Mechanisms and kinetics of autocatalytic decomp of pure liquid,
in nitrobenzene, in vapor phase, catalyzed by water, effect
of inhibition products, solvent effects. (221)

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126. $C_3H_6F_4N_2$ continued

Decomp by heterogeneous dehydrofluorination. (216)(218)(221)

Initial first-order decomp involving HF catalysis in nitrobenzene solution. (224)

Autocatalysis and inhibition of decomp. (215)

HF as autocatalytic agent in decomp. (212)(214)

Thermal decomp in nitrobenzene yields CH_3CN , $CH_3\overset{NF}{\underset{||}{C}}CN$, and FCN or FCH_2CN . (215)

Decomp in aqueous dioxane, diglyme and nitrobenzene; characterization of decomp products. (253)

Dehydrofluorination in aqueous dioxane. (220)

Dehydrofluorination in solution yields $FN=C((H_3)(CN))$ as sole product; with various additives; table. (219)

Mechanisms and kinetics of thermal decomp of neat 1,2-DP. (213)

Structure of intermediates of thermal decomp. (212)

Kinetics of thermal decomp. (50)(51)(52)(244)

Vapor phase thermal decomp. (165)

Activation Parameters dehydrofluorination 30% aqueous diglyme at 50°:
 $\Delta H^\ddagger = 16.7$ kcal/mole; $\Delta F^\ddagger = 25.2$ kcal/mole; $\Delta S^\ddagger = -26.5$ e.u. (256)

Rate of dehydrofluorination, 30% aqueous diglyme:
 $k_{50^\circ} = 6.35 \times 10^{-5} \text{ sec}^{-1}$; $k_{75^\circ} = 4.41 \times 10^{-4} \text{ sec}^{-1}$. (256)

Very Low Pressure Pyrolysis: Compound is half decomposed at 750°. (256)

127. $C_3H_6F_4N_2$

$F_2NCH_2CH_2CH_2NF_2$
(liquid)

Code: 1,3-DP

Impact: No firing up to 170 cm/2 kg wt. (7)

Very sens to electrostatic charge but less so than 2,2- isomer. (7)

Failure diameter transition high to low velocity waves, 1.7 mm. (223)

Failure diameter for low velocity wave is less than 1.2 mm. (223)

Thermal Stability:

DTA: Endo at 138°. (7)

Dehydrofluorination rate, $k = 1.5 \times 10^{-5} \text{ sec}^{-1}$ in 30% dioxane- H_2O at 50°. (223)

Decomp by HF elimination, solution, and gas-phase. (216)

Decomp gases. (216)

Decomp in solution. (219)

Thermal decomp, in nitrobenzene. (244)

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128. $C_3H_6F_4N_2$

$CH_3C(NF_2)_2CH_3$
(liquid)

Code: 2,2-DP

Impact: 53 cm/2 kg. (3)
2.8 kg cm. (51)
2.8 in/1 kg wt; RDX = 10 in; Picatinny. (178)
Greater than 12 in/1 kg wt; propyl nitrate = 4 in; Olin. (178)

Very sens to electrostatic charge and more than 1,3 isomer. (7)

Width of attenuator at 50% gap: 13.2 ± 0.5 mm Plexiglas.

Nitromethane, 11.1 ± 0.8 mm. (219)

Failure diameter transition high to low velocity waves, 4.0 mm. (223)

Failure diameter for low velocity waves is less than 1.6 mm. (223)

Initiates by shock through 95 cm of Plexiglas. (290)

Thermal Stability:

VTS: 28 cc/gm/100 hrs at 90° . (93)
4088 cc/mole/100 hrs at 90° . (93)
Graph, gas evolved vs time. (92)

Wenograd: Temp to 250 μ sec delay, 507° . (115)
Delay time to explosion vs temp, graph, table. (55)

Heat of detonation 1660 cal/gm; NG = 1486 cal/gm. (155)

Activation energy for thermal decomp in nitrobenzene = 36 kcal/mole.
(224)

Activation energy for thermal decomp in gas phase = 45 kcal/mole.
(224)

Very low pressure pyrolysis yields $N_2F_4 + CH_3NF_2 + CH_3CF = NF$.
(224)(220)(219)(223)

Very low pressure pyrolysis: Half decomposed at 550° . (256)

Explosions in vapor pressure vs temp. (48)

Mixtures with ethanol stable at 23° ; slow degradation at 60° . (94)

Mechanism and kinetics of thermal decomp, solution and gas-phase.
(48)(49)(50)(51)(212)(213)(214)(215)

Mechanism and kinetics of thermal decomp of 2,2-DP in
nitrobenzene. (213)

Products of decomp in solution. (214)(215)

Effects of solvent. (213)

Effects of base. (215)

Vapor phase decomposition. (59)(211)

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129. $C_3H_6F_4N_2O$

$CH_3C(NF_2)_2CH_2OH$
(liquid)

Impact: 5.6 kg in; Picatinny.(188)

130. $C_3H_6F_4N_2O$

$F_2NCH_2CH(NF_2)CH_2OH$
(liquid)

Impact: 23 kg cm.(45)
12.3 kg cm; 50% point; Olin.(178)

DuPont Drop Test: 10 in./5 kg wt at 50% point. (79)

Ball Drop: Negative at 45 in. with 8.3 gm ball.(79)

Static Sens: Negative at 77,500 M.E.V. (79)

Thermal Stability:

Hot Bar: Evaporated at 250°.(79)

131. $C_3H_6F_4N_2O_2$

$HOCH_2C(NF_2)_2CH_2OH$
(solid)

Code: DHBP
DPD

Impact: ~10 kg in.(96)
16.5 cm/2 kg wt.; 50% point; mod BuMines.(1)

Friction: Very sensitive.(1)

Spark Sens: Relatively insensitive.(1)

Thermal Stability:

DTA: Endo at 65.7°; exo at 161.4° with shoulder at 131.5°.(95)
No exo observed up to 369°.(1)

VTS: 17 cc/gm/100 hrs at 60°.(96)

132. $C_3H_6F_4N_4O$

$(F_2NCH_2NH-)_2C=O$
(solid)

Code: BDMU

Impact: 10-20 cm.; $\frac{1}{2}$ kg m.s. hammer; NG = 25-30 cm. (243)

Explosion point: 168°.(243)

Thermal Stability:

VTS: 0.3 cc/gm/100 hrs at 60°.(127)

Did not change weight after 7 days at 70°.(120)

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133. $C_3H_6F_4N_6O_4$ Code: BNM $CH_2[N(NO_2)CH_2NF_2]_2$
BDM (solid)
Impact: 18 kg in at 50% point. (97)
Thermal Stability:
VFS: 1.2 cc/gm/120 hr at 60°. (97)
2.0 cc/gm/23 hrs at 90°. (97)
Composition of decomp. gases. (98)
134. $C_3H_6F_6N_4$ Code: TDMA $N(CH_2NF_2)_3$
(liquid)
Impact: 10-20 cm; $\frac{1}{2}$ kg m.s. hammer. (121)
Explosion Point: Greater than 166°. (127)
Thermal Stability:
DTA: Endo at 180°. (127)
No decomp after storage in Pyrex at ambient temp for 3 months. (127)
Decomp at 60°. (127)
Autocatalytic decomp. (123)
135. $C_3H_7BrF_6N_4O$ Code: INFO-631 Br $(NF_2)_3COC_2H_4NH_3Br$
(solid)
Impact: 8 cm; NOL drop height. (146)
Shock Tube Test: graph. (246)
136. $C_3H_7ClF_6N_4O$ Code: INFO-631 Cl $(NF_2)_3COC_2H_4NH_3Cl$
(solid)
Impact: 4.9 cm; NOL drop height. (147)

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137. $C_3H_7ClF_6N_4O_5$

$(NF_2)_3COCH_2CH_2NH_3ClO_4$

Code: INFO-635P

(solid)

INFO-635

Impact: 3 cm/2 kg wt.; RDX = 30-35 cm/2 kg wt.; BuMines. (240)
7.5-11 kg cm, depending on treatment. table; Olin.(240)
Effects of 11 liquids, table.(113)
10-19 kg cm; PbN_6 = 8-12 kg cm; Teteryl = 30 kg cm;
Picatinny.(114)
20 kg cm; PbN_6 = 33 kg cm; Teteryl = >85 kg cm; mod.
Picatinny.(114)
Varying with treatment, table.(112)
20 kg cm; Esso Bruceton.(112)
8.6 cm/2 kg wt; NG = 11-13 cm; HMX = 50 cm; zero
initiation level. (240)
About 30 kg cm. (140)
2.4 cm; NOL drop height.(246)
5.0 kg cm at 50% point.(240)

Friction: 1 (+), 1 (-) at 0 gm, 500 rpm (extremely sens);
AGC rotational tester.(240)
With varying tools, table.(113)
Hardness 5.5; PbN_6 = hardness 4; Teteryl = >hardness 10.(114)
Negative with bare tools; Esso screw test.(112)
Positive with 100 mm glass; Esso screw test.(112)
Varying with treatment; Esso screw test.(112)
Less than 250 rpm.(240)

Spark: Positive at 0.05 joules; negative at 0.01 joules.(240)
Greater than 1.8 joules.(114)
0.002 joules; HMX = 12.5 joules; NOL test.(63)

Shock Tube Sens: Varying with temp, graph.(245)

Thermal Stability:

DTA: Indicates INFO-635 unchanged chemically after treatment
with Freon-11 and Freon-113.(240)
Decomp start at 150° , peak at 182° .(63)
Exo at 182° .(143)
Endo at 150° (crystal phase transition), explode at 193° .(193)
Exo start at 178° , ignited at 208° .(20)

Autoignition temp, 5 sec: 249; Teteryl = 258.(114)
Autoignition temp, 10 sec: 236; Teteryl = 240.(114)

Taliani: No decomp for 3 days at 70° , graph.(245)
Varying with purity, graph; modified test.(247)
No cc/gm/23 hrs at 93° but increased in oxidizing
power. (240)

VTS: Graph of pressure rise vs time.(20)
In Teflon: 0.43 cc/gm/100 hrs at 60° ; 1.6 cc/gm/100 hrs
at 75° ; 6.1 cc/gm/100 hrs at 90° .(109)
In glass: 0.35 cc/gm/100 hrs at 60° ; 1.3 cc/gm/100 hrs
at 75° ; 4.2 cc/gm/100 hrs at 90° .(109)

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137. $C_3H_7ClF_6N_4O_5$ (continued)

Hot Stage: Bubbling at 110° .(141)

Stability varying with purity, graph.(143)(246)

No decomp below 140° .(141)

No decomp at $60-70^\circ$ for 10 days.(63)

Decomp began after 4 days at $80-90^\circ$.(63)

The free amine decomposes rapidly at ambient temp. (62)

Not stable in molten state. (116)

Dry solids (crude INFO-635) show no decomp at 65° for 4 wks.(240)

Desensitization: With amine salts; graph of 50% impact point vs percent additive.(115)

With additives, table.(113)(116)

Washing with Freon decreased sensitivity.(240)

In various solvents.(245)

Pure compound more sensitive than crude.(240)

Various attempts to desensitize.(240)

Tables on desensitization.(114)

Handleability: Remote handling without difficulty.(105)

Incident: 11 gm of INFO-635, vacuum dried overnight 25° , detonated while being held in remote manipulators.(240)

Decomp at 160° , 170° in air and vacuum.(64)

Thermal decomposition.(63)

Thermal decomposition of salt and free amine.(62)

Decomposition: Metal vs Teflon containers. (246)

Decomposition. (59)(60)(61)

Kinetics of solution decomposition. (62)

138. $C_3H_7F_4N_3O_2S$

$H_3CSO_2N(CH_2NF_2)_2$
(solid)

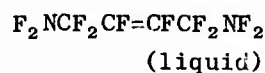
Impact: 30-40 cm; $\frac{1}{2}$ kg m.s. hammer.(127)

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139. $C_3H_7F_6N_5O_4$ $(NF_2)_3COC_2H_4NH_3NO_3$
Code: INFO-634 N (solid)
Impact: 7.6 cm; NOL drop height. (146)
140. $C_3H_8ClF_4N_3O_4$ $F_2NCH_2CH(NF_2)CH_2NH_2HClO_4$
Code: AAPA (solid)
Impact: 20 kg cm; Picatinny. (108)
Spark: Greater than 1.8 joules. (108)
Friction: Hardness 4. (108)
Thermal Stability:
VTS: 2.0 cc/gm/100 hrs at 60°. (108)
141. $C_3H_8ClF_4N_3O_5$ $F_2NCH_2CH(NF_2)CH_2ONH_3ClO_4$
(solid)
VTS: 2.0 cc/gm/100 hrs at 60°. (108)
142. $C_3H_8ClF_5N_4O_5$ $FHNC(NF_2)_2OCH_2CH_2NH_3ClO_4$
Code: INFO-535 (solid)
Impact: Less than 1 kg cm. (143)
Greater than 15 kg cm; 1 kg wt; Olin. (29)
Friction: Negative at Hardness 10. (29)
143. $C_4F_{10}N_2$ $C_3F_7C(=NF)NF_2$
(liquid)
No decomp. in sev. wks. at -20°. (207)

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144. $C_4F_{10}N_2$

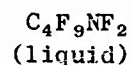


Thermal Stability:

VTs: 0.1 cc/gm/100 hrs at 90°. (94)

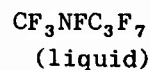
Mixtures with ethanol stable at 23°, unstable at 60° after 72 hrs.
(94)

145. $C_4F_{11}N$



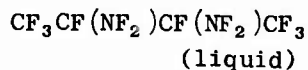
Gas phase pyrolysis yields C_3F_7CN . (118)

146. $C_4F_{11}N$



Gas phase thermal decomposition. (118)

147. $C_4F_{12}N_2$



Impact: ~ 8 kg in. (231)

Thermal Stability:

VTs: 9 cc/gm/100 hrs at 23°. (95)

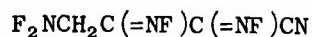
3.3 cc/gm/100 hrs at 90°. (94)

Very little decomp. to 150°. (231)

Thermally decomposed at 200°. (231)

Wenograd test: Temp at 250 μ sec delay, 625°. (155)

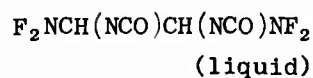
148. $C_4H_2F_4N_4$



Unstable. (96)

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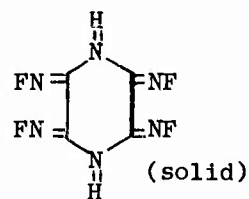
149. $C_4H_2F_4N_4O_2$



VTS: 2 cc/gm/100 hrs at 90°. (93)
428 cc/mole/100 hrs at 90°. (93)

150. $C_4H_2F_4N_6$

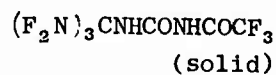
Code: TFP



Impact: 5 to 10 cm; $\frac{1}{2}$ kg m.s. hammer. (126)

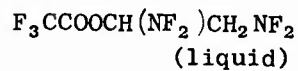
Explosion point: 244.5°. (127)

151. $C_4H_2F_9N_5O_2$



Dry solid slowly decomp. to Tris U at 25° for 38 days. (42)

152. $C_4H_3F_7N_2O_2$



Impact: Greater than 38 kg in.; Picatinny. (179)

Thermal Stability:

Thermal decomp; table. (179)

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153. $C_4H_3F_{12}N_9O_2$

$[(F_2N)_3CNHCO-]_2NH$
(solid)

Code: BT-Biuret

Impact: 10 to 20 cm; $\frac{1}{2}$ kg wt. (35)

15 kg cm. (37)

About 5 cm; 0% fires; 2 kg wt. (39)

Desensitization: 0 out of 10 times fired at 50 cm/2 kg wt; 8% solution in acetonitrile. (39)

Thermal Stability:

DTA: Not reproducible - exo ~ 90 to 100; max. 162 to 171. (35)

Recrystallized sample: 15.3 cc/gm for 150 min. at 70°. (37)

Taliansi: 34.1 cc/gm / 5 $\frac{1}{2}$ hrs at 70° in N₂ atmosphere. (37)

TGA: Wt. loss start at 100°, explosion at 180°. (37)

154. $C_4H_4F_4N_2O$

$CH_2=CH O C(NF_2)=CHNF_2$
(liquid)

Impact: 12.5 kg cm. (45)

155. $C_4H_4F_4N_2O$

 $(NF_2)_2$
(liquid)

Impact: 5 kg in at 50% point. (91)

25 kg in at 50% point diluted at 50% CCl₄. (91)

Thermal Stability:

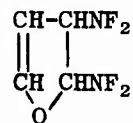
Discolored and formed gummy precipitate at ambient temp under N₂. (91)

Degradation: Reduced by dilution with Freon 11. (91)

Eliminated by dilution with Freon 11 and storage at 0°F. (91)

Desensitization: Graph of impact vs wt % of CCl₄. (91)

156. $C_4H_4F_4N_2O$

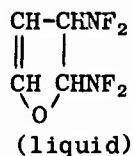

(liquid)

Impact: 12.5 kg cm. (45)

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157. $C_4H_4F_4N_2O$

Code: Trans isomer

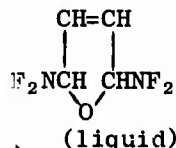


(liquid)

Thermal Stability:

VTS: 4 cc/gm/100 hrs at 90°. (93)
688 cc/mole/100 hrs at 90°. (93)
Graph of gas evolved vs time. (90)
Trans isomer more stable than cis. (93)

158. $C_4H_4F_4N_2O$



(liquid)

DuPont Drop Test: 12 kg cm at 50% point. (79)

Ball Drop: Negative at 45 in with 8.3 gm ball. (79)

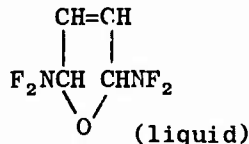
Static Sens: Shot at 36,400 M.E.V. (79)

Thermal Stability:

Copper Block: Boil-off at 140°. (79)

159. $C_4H_4F_4N_2O$

Code: Cis isomer



(liquid)

Impact: 5 kg in at 50% point; 21 kg in diluted in 50% CCl_4 ;
Picatinny. (91)

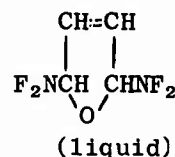
Thermal Stability:

VTS: 2 cc/gm/100 hrs at 90°. (93)
344 cc/mole/100 hrs at 90°. (93)
Graph of gas evolved vs time. (90)

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160. $C_4H_4F_4N_2O$

Code: Trans isomer



(liquid)

Impact: 5 kg in at 50% point; 25 kg in diluted to 50% CCl_4 ; Picatinny.(91)

Thermal Stability:

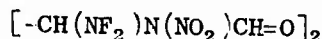
VTS: 0.6 cc/gm/100 hrs at 90° .(93)

103 cc/mole/100 hrs at 90° .(93)

Graph of gas evolved vs time.(90)

Trans isomer more stable than cis.(91)

161. $C_4H_4F_4N_6O_6$



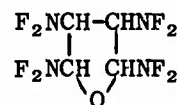
Code: DFBEDNA

(solid)

Decomposition: Composition of gases evolved.(98)

162. $C_4H_4F_8N_4O$

Code: TDTF
TDTHF
THFA



(liquid)

Impact: 2.3 kg cm.(44)

Table of impact vs % volume IBA and TDTF.(44)

1.5-2.5 kg cm at 50% point; 126 kg cm, diluted; Olin.(47)

About 5 kg in at 50% point. 13 kg in diluted in 50% CCl_4 .(91)

DuPont Drop Test: 7 kg cm at 50% point.(80)

Ball Drop: Negative at 10 in with 8.3 gm ball.(80)

Base Load: No. 3 lead plate.(80)

Static Sens: Detonated at 18,250 M.E.V.(80)

Thermal Stability:

DTA: Exo at 193° ; modified bomb.(44)

Exo at $125-155^\circ$.(94)

Copper Block: Boil-off at 250° .(80)

Hot Bar: Boil-off at 250° .(80)

VTS: 1 cc/gm/100 hrs at 90° .(93)

276 cc/mole/100 hrs at 90° .(93)

Graph: Gas evolved vs time.(91)

Gas evolved vs time for three isomers.(90)

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162. $C_4H_4F_8N_4O$ (continued)

Not stable in glass but storable in polyethylene.(44)

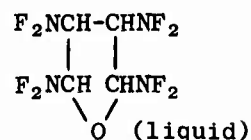
Decomp immediately in ethanol at 23° and 60°.(94)

Exploded when injected into a 300°F GLC chamber.(47)

Desensitization: Graph of impact vs wt % CCl_4 .(91)

163. $C_4H_4F_8N_4O$

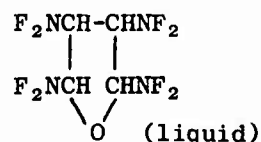
Code: THFA, trans, trans isomer



Impact: 1 kg in at 50% point. 20 kg in diluted to 50% CCl_4 ;
Picatinny.(91)

164. $C_4H_4F_8N_4O$

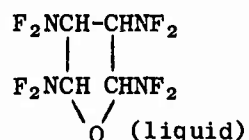
Code: THFA, cis, cis isomer



Impact: 1 kg in at 50% point. 15 kg in diluted to 50% CCl_4 ;
Picatinny.(91)

165. $C_4H_4F_8N_4O$

Code: THFA, cis, trans isomer

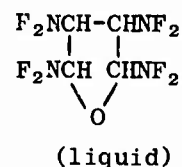


Impact: 3 kg in at 50% point. 18 kg in diluted to 50% CCl_4 ;
Picatinny.(91)

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166. $C_4H_4F_8N_4O$

Code: THFA, 4.0 RT isomer*



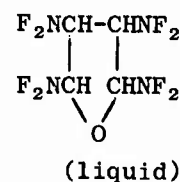
Thermal Stability:

VTS: 140 cc/gm/100 hrs at 90°. (93)
24,640 cc/mole/100 hrs at 90°. (93)

*GLC Retention Time designation.

167. $C_4H_4F_8N_4O$

Code: THFA, 6.0 RT isomer*



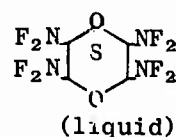
Thermal Stability:

VTS: 12 cc/gm/100 hrs at 90°. (93)
2112 cc/mole/100 hrs at 90°. (93)

*GLC Retention Time designation.

168. $C_4H_4F_8N_4O_2$

Code: TDD



Impact: 7.5 kg cm. (45)

3 kg in; 1.4% of bis-impurity. (89)
5 to 10 cm; $\frac{1}{2}$ kg m.s. hammer. (120)

Desensitization in CH_2Cl_2 , table. (120)

Thermal Stability:

VTS: Initial rate 3.5 cc/gm/100 hrs; steady rate,
0.4 ml/gm/100 hrs. (124)

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169. $C_4H_4F_{12}N_{10}O_2$

$[(F_2N)_3CNHCO]_2NH$
(solid)

Code: BTBU
BT-Biurea

Impact: 8 kg in. (99)
About 1 cm; 2 kg wt; 0% fires. (39)

Thermal Stability:

DTA: Exo at 157° . (39)
Exo at 136° . (100)

VTS: 17 cc/gm/20 hrs at 60° . (100)
37 cc/gm/42 hrs at 60° . (100)
90 cc/gm/100 hrs at 60° . (100)

170. $C_4H_5ClF_4N_2O$

$F_2NCH_2C(NF_2)(CH_3)COCl$
(liquid)

Stable when stored at ambient conditions. (181)

171. $C_4H_5F_2NO_2$

$F_2NCH_2OOCCH=CH_2$
(liquid)

Code: NFMA

Impact: Greater than 38 kg in; RDX = 9.5; Picatinny. (179)

172. $C_4H_5F_4N_3$

$CH_3CH(NF_2)CH(NF_2)CN$
(liquid)

Wenograd: Temperature to 250 μ sec delay, 661° . (155)

173a. $C_4H_5F_4N_5O_6$

$(O_2N)_3CCH_2CH_2CH(NF_2)_2$
(liquid)

Impact: 4 kg cm. (286)

Static: Positive at 0.05 joule. (286)

Thermal Stability:

DTA: Exo at 210° . (286)

Explosion occurred during elemental analyses. (205)

173b. $C_4H_5F_6N_3O_2$

$CH_3CHCH_2OC(NF_2)_3$
(liquid)

Code: FA-G

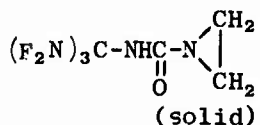
Impact: Less than 1 kg in. (284)

Friction Screw: Positive at Hardness 3. (284)

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174. $C_4H_5F_6N_5O$



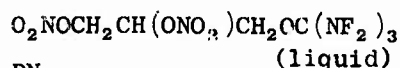
Thermal Stability:

Sample detonated after standing 10 min at 25°. (39)

Stable in $CHCl_3$ at -50°. (39)

Polymerized upon warming to 25°. (35)

175. $C_4H_5F_6N_5O_7$



Code: FA-C-DN

Impact: 4 kg cm. (109)

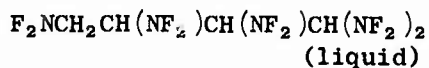
Friction: Positive with bare tools. (109)

Spark: Negative. (109)

Thermal Stability:

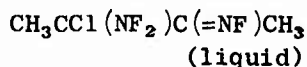
VTs: Less than 0.10 cc/gm/100 hrs at 60°. (109)

176. $C_4H_5F_{10}N_5$



Extremely unstable. (96)

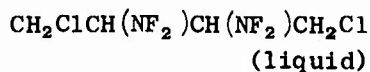
177. $C_4H_6ClF_3N_2$



Code: MNFP

DTA: No reaction before b.p. (197)

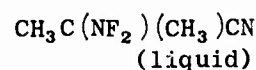
178. $C_4H_6Cl_2F_4N_2$



Impact: 26 kg in. (87)

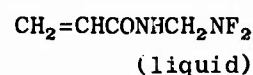
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179. $C_4H_6F_2N_2$



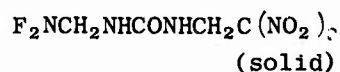
DTA: Exo at 288; modified bomb. (44)

180. $C_4H_5F_2N_2O$



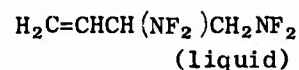
Impact: Greater than 200 cm; $\frac{1}{2}$ kg m.s. hammer. (127)

181. $C_4H_6F_2N_6O_7$



VTS: 0.2 ml/gm/100 hrs at 60°. (127)

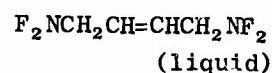
182. $C_4H_6F_4N_2$



Thermal Stability:

VTS: 1.5 cc/gm/100 hrs at 90°. (94)
237 cc/mole/100 hrs at 90°. (94)

183. $C_4H_6F_4N_2$

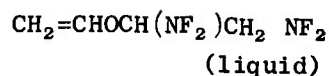


Thermal Stability:

VTS: 70 cc/gm/100 hrs at 23°. (95)
2.3 cc/gm/100 hrs at 90°. (94)
279 cc/mole/100 hrs at 90°. (93)

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181. $C_4H_6F_4N_2O$



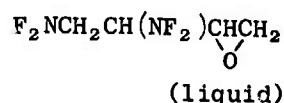
DuPont Drop Test: 1 in/5 kg wt at 50% point. (79)

Ball Drop: Negative at 45 in. with 8.3 gm ball. (79)

Thermal Stability:

Hot Bar: No reaction at 250°. (79)

185. $C_4H_6F_4N_2O$



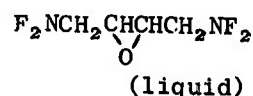
Impact: 5 kg cm. (201)

Thermal Stability:

0.23 cc/gm/100 hrs at 60° for 699 hr. (202)

78 cc/gm/100 hrs at 100° for 123 hr. (202)

186. $C_4H_6F_4N_2O$



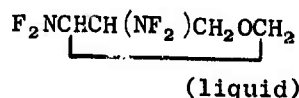
Impact: Positive at 10 kg cm and negative at 15 kg cm. (201)

Thermal Stability:

0.25 cc/gm/100 hrs at 60° for 1563 hrs. (202)

6.3 cc/gm/10 hrs at 100° for 219 hrs. (202)

187. $C_4H_6F_4N_2O$

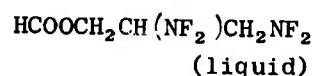


Code: BDTF

Poor storage stability. (71)

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188. $C_4H_6F_4N_2O_2$



Code: AFA
BDPF

Impact: 4.5 kg cm at 50% point; Olin. (47)

35 kg in; 50% fire; RDX = 15.5; Picatinny. (80)

DuPont Drop Test: 13 in/5 kg wt at 50% point; NG = 6 in/5 kg wt. (82)

Ball Drop: Negative at 45 in with 8.3 gm ball. (82)

Static Sens: Negative at 77,500 M.E.V. (82)

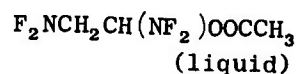
Thermal Stability:

Autoignition: Boil off at 250°. (47)

Copper Block: Boiled away. (82)

Hot Bar: Boil off at 250°. (82)

189. $C_4H_6F_4N_2O_2$



DuPont Drop Test: Greater than 480 kg cm. (79)

Impact: Greater than 480 kg cm. (45)

Ball Drop: Negative at 45 in with 8.3 gm ball. (79)

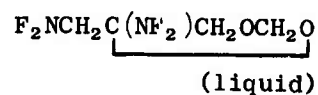
Static Sens: Negative at 77,500 M.E.V. (79)

Thermal Stability:

Copper Block: Boil away up to 250°. (79)

Hot Bar: Boil away at 250°. (79)

190. $C_4H_6F_4N_2O_2$



DuPont Drop Test: 24 kg cm at 50% point. (79)

Ball Drop: Negative at 45 in with 8.3 gm ball. (79)

Base Load: No. 5 lead plate. (79)

Static Sens: Shot at 41,600 M.E.V. (239)

Thermal Stability:

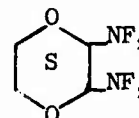
Copper Block: Negative up to 250°. (79)

Hot Bar: Negative at 250°. (79)

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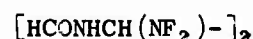
191. $C_4H_6F_4N_2O_2$



Impact: 40 to 60 cm; $\frac{1}{2}$ kg m.s. hammer. (127)

(liquid)

192. $C_4H_6F_4N_4O_2$



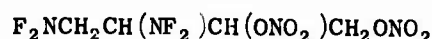
(liquid)

Impact: 20 to 30 cm; $\frac{1}{2}$ kg m.s. hammer. (122)

Thermal Stability:

Explosion point: 169° . (122)

193. $C_4H_6F_4N_4O_6$



(liquid)

Impact: 7 kg cm. (79)

2 cm/2 kg wt; saturated on glass cloth. (130)

DuPont Drop Test: 8 kg cm at 50% point. (79)

Ball Drop: Negative at 22 in, shot at 26 in with 8.3 gm ball. (79)

Base Load: No. 2 lead plate. (79)

Static Sens: Shot at 41,600 M.E.V. (79)

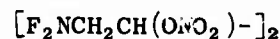
Thermal Stability:

Autoignition Temp: 191° . (130)

Hot Bar: Evaporation at 250° ; no residue. (79)

Copper Block: Boil off at greater than 250° . (79)

194. $C_4H_6F_4N_4O_6$



(liquid)

Impact: 1 cm/2 kg wt; saturated on glass cloth. (130)

Thermal Stability:

Autoignition temp: 195° . (130)

Good stability in polyethylene. Minor change in IR after 30 days. (129)

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195. $C_4H_6F_4N_4O_6$

$[O_2NOCH_2CH(NF_2)]_2$
(liquid)

Code: BDBD

Impact: 2.0 kg cm; 50% point; 117 kg cm diluted in $CHCl_3$; Olin. (47)

DuPont Drop Test: 3 kg cm at 50% point. (239)

Ball Drop: Detonated at 10 in with 8.3 gm ball. (239)

Base Load Test: No. 2 lead plat. (239)

Can be desensitized. (46)

Thermal Stability:

DTA: Minor decomp at 119° ; peak 180° . (70)

VTS: No decomp. at $30^\circ/120$ hrs. (70)

Autoignition Temp: 225° . (47)

Copper Block: Fume-off at 250° . (239)

Hot Bar: Fumed at 250° , then detonated. (239)

196. $C_4H_6F_5N_3O_3$

$HFNC(NF_2)_2OCH_2COOCH_3$
(liquid)

Thermal Stability:

Stable in acetonitrile 20 hrs at 50° . (141)

Stable in acetonitrile 7 days at 25° . (141)

Decomp in 7 days in aqueous trifluoroethanol. (141)

197. $C_4H_6F_6N_4O_3$

$(F_2N)_3CON=C(OCH_3)_2$

Four out of six attempts at elemental analysis ended in explosion. (250)

198. $C_4H_6F_8N_4$

Code: TDB
TBA

$[F_2NCH_2CH(NF_2)]_2$
(liquid)

Impact: 0-20 kg cm. (45)

DuPont Drop Test: 20 kg cm to 50% point. (83)

Heat of Detonation: 1570 cal/gm; NG = 1486 cal/gm. (155)

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198. $C_4H_6F_8N_4$ (continued)

Thermal Stability:

Wenograd: Temp at 250 μ sec delay, 600°. (155)

Mixtures with ethanol; slow decomp to 72 hrs at 23°. (94)
Decomp in 24 hrs at 60°. (94)

VTS: 1.0 cc/gm/100 hrs at 90°. (94)

Graph: Gas evolved vs time. (94)

GC pure sample; no gas evolution after 96 hrs at 90°. (97)

Bicarbonate wash improves thermal stability; table. (97)

Mixtures with NP. (95)

199. $C_4H_6F_8N_4O$

$[F_2NCH_2CH(NF_2)-]_2O$
(liquid)

Code: TDEE

Impact: 10 to 12 kg in. (45)

2 to 3 kg cm at 50% point; Olin. (178)

DuPont Drop Test: 6 kg cm at 50% point. (83)

Ball Drop: Negative at 8 in; detonated at 10 in with 8.3 gm ball. (83)

Base Load Test: No. 1 lead plate. (83)

Static Sens: Negative at 28,300 M.E.V. (83)

Heat of Detonation: 1490 cal/gm; NG = 1486 cal/gm. (155)

Thermal Stability:

Wenograd: Temp at 250 μ sec delay, 563°. (155)

Hot Bar: Evaporation after 8.3 sec at 250°. (83)

200. $C_4H_6F_8N_4O$

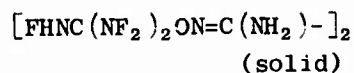
$F_2NCH_2CH(NF_2)CH(NF_2)CH(OH)NF_2$
(liquid)

Unstable by virtue of $\begin{array}{c} H \\ | \\ -C- \\ | \\ NF_2 \end{array} \begin{array}{c} OH \\ | \end{array}$ structure. (83)

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201. $C_4H_6F_{10}N_{10}O_2$



Impact: 3.6 kg cm. (138)

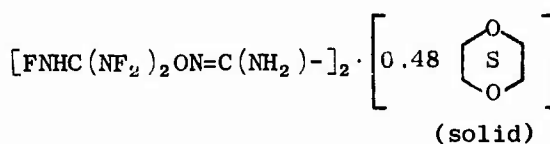
Explosion occurred when scraped with spatula. (138)

Thermal Stability:

Turns yellow slowly over 10-hr period at 25° . (138)

Stable indefinitely at -78° . (138)

202. $C_4H_6F_{10}N_{10}O_2 \cdot (0.48)C_4H_8O_2$

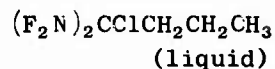


Impact: 1.8 cm/2 kg. (137)

Thermal Stability:

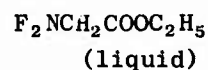
Decomposes above 90° . (137)

203. $C_4H_7ClF_4N_2$



Two attempted F analyses resulted in explosions. (13)

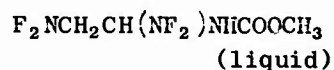
204. $C_4H_7F_2NO_2$



Thermal Stability:

70% pure material undergoes dehydrofluorination at $60-70^\circ$. (10)

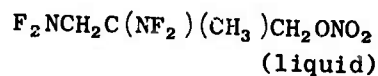
205. $C_4H_7F_4N_3O_2$



Wenograd: Temp at 250 μ sec delay, 655° . (155)

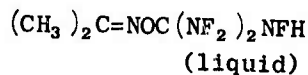
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206. $C_4H_7F_4N_3O_3$



Impact: 3.5 kg cm; modified Olin. (180)
5.6 kg in; RDX = 20 kg in; Picatinny. (180)

207. $C_4H_7F_5N_4O$

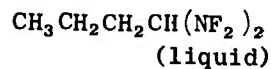


Impact: 1.8 cm/2 kg wt. (137)

Thermal Stability:

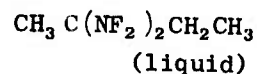
Decomposes slowly at 60° yielding HNF_2 + PFG. (137)

208. $C_4H_8F_4N_2$



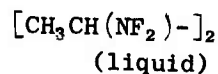
Impact: 2.5 kg cm. (152)
5.6 kg in.; Picatinny. (152)

209. $C_4H_8F_4N_2$



Impact: 4.0 kg in.; Picatinny. (190)

210. $C_4H_8F_4N_2$



Code: 2,3-DB

Impact: 32 kg in. (87)

Thermal Stability:

DTA: Exo at 264°; modified bomb. (44)

VTS: 25 cc/gm/80 hrs at 23°. (95)

1.3 cc/gm/100 hrs at 90°. (94)

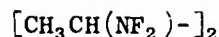
Effect of temp. (95)

Mixtures with ethanol stable at 23°, unstable at 60°. (94)

Decomp in aqueous solution produces $CH_3-\overset{\overset{||}{NF}}{C}-\overset{\overset{||}{NF}}{C}-CH_3$. (220)

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211. $C_4H_8F_4N_2$



Code: 2,3-DB-1*

(liquid)

Thermal Stability:

Rate constant for total dehydrofluorination in 30% aqueous dioxane, 50°: $8.77 \times 10^{-5} \text{ sec}^{-1}$. (221)

Rate constant for total dehydrofluorination in 30% aqueous diglyme, 50°: $1.68 \times 10^{-4} \text{ sec}^{-1}$. (258)

Activation parameters for dehydrofluorination in 30% aqueous diglyme, 50°:
 $\Delta H^\ddagger = 15. - \text{kcal/mole}$; $\Delta F^\ddagger = 24.6 \text{ kcal/mole}$;
 $\Delta S^\ddagger = -29.3 \text{ e.u.}$ (258)

Dehydrofluorination in aqueous dioxane and diglyme; comparison of stereoisomers. (221)

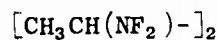
Autocatalytic decomp in nitrobenzene. (221)

Mechanisms and kinetics of dehydrofluorination in various aqueous solvents. (224)

Dehydrofluorination in aqueous diglyme producing isomers of 2,3-bis(N-fluorimino)butane. (223)

*Stereoisomer

212. $C_4H_8F_4N_2$



Code: 2,3-DB-2*

(liquid)

Thermal Stability:

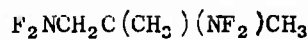
Dehydrofluorination in aqueous dioxane and diglyme. (221)

Dehydrofluorination in aqueous diglyme; identification of products. (223)

Dehydrofluorination rate constant in 30% aqueous dioxane at 50° = $7.64 \times 10^{-5} \text{ sec}^{-1}$. (221)

*Stereoisomer

213. $C_4H_8F_4N_2$



Code: IBA

(liquid)

Impact: 36.8 kg cm. (51)

5.7 kg cm at 50% point; Olin. (178)

15 kg in at 50% fire level; RDX = 12.9 kg in;
Picatinny. (177)

11.5 kg cm; JANAF STD. (44)

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213. $C_4H_8F_4N_2$ (continued)

Impact vs % volume IBA and TDTF, table. (44)

Card Gap: Deformation at 10 cards and above. (44)

Width of attenuator at 50% gap: 14.4 ± 0.2 mm plexiglass;
nitromethane = 11.1 ± 0.8 mm. (219)

Failure diameter transition, high to low velocity waves, 9.0 mm. (258)

Thermal Stability:

DTA: Exo at 238° ; modified bomb. (44)

Slight discoloration at 100 hrs/ 120° /1 atmosphere, sealed. (177)

Desensitization in acetone in methylene chloride. (177)

Activation energy for thermal decomp in nitrobenzene from
 $165-200^\circ = 31$ kcal/mole. (224)

Activation energy for thermal decomp in gas phase from
 $165-200^\circ = 47$ kcal/mole. (224)

Dehydrofluorination rate, $k = 2 \times 10^{-5} \text{ sec}^{-1}$ in 30% dioxane- H_2O
at 50° . (223)

Initial first-order decomp involving HF catalysis in nitrobenzene
solution over temp range $175-200^\circ$.

Decomp in aqueous dioxane at 50° . (220)

Kinetics of autocatalytic thermal decomp. (215)

Decomposition kinetics. (221)

Decomposition products. (59)(44)

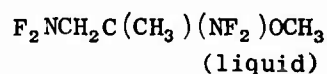
Decomposition constant. (59)

Gas phase, thermal decomposition. (50)(59)(186)(194)

Activation Parameters, dehydrofluorination in 30% aqueous diglyme at 50° :
 $\Delta H^\ddagger = 14.8$ kcal/mole; $\Delta F^\ddagger = 26.0$ kcal/mole; $\Delta S^\ddagger$: -34.6 e.u. (258)

Rate of decomposition for dehydrofluorination in 30% aqueous diglyme:
 $k_{50^\circ} = 1.7 \times 10^{-5} \text{ sec}^{-1}$; $k_{75^\circ} = 1.0 \times 10^{-4} \text{ sec}^{-1}$. (258)

214. $C_4H_8F_4N_2O$



Thermal Stability:

VTS: 12.3 cc/gm/100 hrs at 110° for 244 hrs; 98.1% pure;
graph. (201)

Desensitization: Stability greatly diminished by impurities. (201)

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215. $C_4H_8F_4N_2O_2$

$[CH_3OCH(NF_2)-]_2$
(liquid)

Impact: 40-60 cm; $\frac{1}{2}$ kg m.s. hammer. (127)

Thermal Stability:

DTA: No exo. (73)

No change after 6 hrs/100°. (73)

216. $C_4H_8F_4N_2O_2$

$[HOCH_2CH(NF_2)-]_2$
(liquid)

Thermal Stability:

VTS: 27 cc/gm/100 hrs at 60°. (93)

5,184 cc/mole/100 hrs at 60°. (93)

217. $C_4H_8F_4N_6O_4$

$[-CH_2N(NO_2)CH_2NF_2]_2$
(solid)

Impact: 20 kg in. (241)

Thermal Stability:

VTS: 30 cc/gm/100 hrs at 60°. (241)

218. $C_4H_9FN_2O_2$

$CH_3CH_2CH_2CH_2NFNO_2$
(liquid)

Impact: 25 cm/2 kg (impure sample); RDX = 30 cm/2 kg. (5)

Thermal Stability:

When heated to 90°, gassed, exo reaction; dense fumes. (93)

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219. $C_4H_9FN_2O_2$

$(H_3C)_2CHCH_2NFNO_2$
(liquid)

Decomposition kinetics in ethylcyclohexane. (153)

220. $C_4H_9FN_2O_2$

$(H_3C)_3CNFNO_2$
(liquid)

Decomposition kinetics in solution. (153)

221a. $C_4H_9F_2N$

$(H_3C)_3CNF_2$
(liquid)

Impact: Fired once out of four at 39 kg in; RDX = 10 kg in. (176)

Thermal Stability:

VTS: 30.0 cc/gm/100 hrs at 90°. (93)
3270/mole/100 hrs at 90°. (93)

Thermal decomposition, gas-phase. (192)(196)(258)

221b. $C_4H_9F_2N$

$CH_3CH_2CH_2CH_2NF_2$
(liquid)

Thermal Stability:

Gas-phase, thermal decomposition. (192)

222. $C_4H_{10}BF_2N$

$(C_2H_5)_2BNF_2$
(liquid)

Impact: Greater than 152 kg cm. (45)
Not sensitive. (92)

Autoignition: Does not ignite. (92)

Thermal Stability:

DTA: No exo to 600°. (92)

223. $C_4H_{10}ClF_4N_3O_4$

$F_2NCH_2CH(NF_2)CH_2CH_2NH_2HClO_4$
(solid)

Thermal Stability:

VTS: 1.2 cc/gm/100 hrs at 60°. (108)

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224. $C_4H_{11}ClFNO_5$

$FNH_3ClO_4 \cdot C_4H_8O$
(liquid)

Thermal Stability:

Stable for sev days in dry atmosphere at 25° . (11)

Decomp. rapidly at 100° . (11)

Decomp. in vacuum ($20^\circ/5mm$) in less than 5 hr. (11)

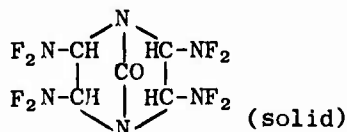
225. $C_5F_{11}N$

$NF(CF_2)_4CF_2$
(liquid)

Pyrolytic decomposition, gas-phase. (118)

226. $C_5H_4F_8N_6O$

Code: TDEKP



Impact: 5-10 cm; $\frac{1}{2}$ kg m.s. hammer; NG = 25-30 cm. (243)

Thermal Stability:

Explosion point 136° . (243)

Thermal Decomp: Initial rapid pressure rises during first 50 hrs then constant slower rate. (123)

227. $C_5H_4F_9N_3O_3$

$CF_3COOCH_2CH_2OC(NF_2)_3$
(liquid)

Decomposition in hot tube yields $N_2F_4 + CF_3NF_2, COF_2,$
and $CH_3COOCH_2CH_2F$. (249)

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228. $C_5H_4F_{12}N_8O_6$ $(F_2N)_3COCH_2C(NO_2)_2CH_2OC(NF_2)_3$
Code: FA-AD (liquid)
Shock: About 2 kg in. (99)
Thermal Stability:
DTA: Slow decomp at 165°, explosion at 212°. (99)
VTS: 7.5, 5.7 cc/gm/6 days at 60°. (99)
229. $C_5H_4F_{16}N_8O_2$ $(F_2N)_3COCH_2C(NF_2)_2CH_2OC(NF_2)_3$
Code: FA-GD (liquid)
Impact: Estimated as less than 1 kg in. (99)
2.5 kg in. (284)
Thermal Stability:
No gas evolved after 1 wk at 60°. (99)
DTA: Decomp begins at 207°, maximum at 234°. (99)
230. $C_5H_5F_7N_2O_2$ $F_2NCH_2CH(NF_2)CH_2OOCCH_2F$
(liquid)
Impact: 8.8 kg cm at 50% point; Olin. (178)
231. $C_5H_6F_4N_2O_2$ $F_2NCH_2CH(NF_2)OOCCH=CH_2$
(liquid)
Impact: Greater than 25 kg in; RDX = 9.5 kg in; Picatinny. (239)
232. $C_5H_6F_4N_2O_3$ $F_2NCH_2CH(NF_2)CHCH_2OC(=O)O$
(liquid)
DuPont Drop Test: Greater than 480 kg cm. (79)
Ball Drop: Negative at 45 in with 8.3 gm ball. (79)
Static Sens: Negative at 77,500 M.E.V. (79)
Thermal Stability:
Copper Block: Fume-off at 250°. (79)
Hot Bar: Fume-off at 250°. (79)
No change after 2 months. (87)

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233. $C_5H_6F_4N_6O_8$

$(O_2N)_3CCH_2OOCNHCH(NF_2)CH_2NF_2$
(liquid)

Impact: 10-12 kg in.(87)

DuPont Drop Test: Positive at 12 in at 50% point; 2 kg wt.(79)

Static Sens: Negative at 77,500 M.E.V.(79)

Thermal Stability:

Hot Bar: Fumed-off at 250° .(79)

No change after 2 months.(87)

234. $C_5H_6F_6N_8O_9$

$(NF_2)_3COCH_2CH_2N(NO_2)CH_2C(NO_2)_3$
(solid)

Code: FA-TNENE

Impact: 3.5-35 kg cm.(109)

6.5 cm NOL drop height.(146)

Spark: Greater than 1.0 joule.(109)

Friction Screw: Negative at Hardness 10. (109)

Thermal Stability:

Various treatment of samples cause VTS to range from
0.35 to 2 cc/gm at 60° in 100 hrs. (106)

VTS: No evolution/100 hrs at 60° .(109)

0.1 cc/gm/100 hrs at 75° .(109)

8.9-9.2 cc/gm/100 hrs at 90° .(109)

Manual handling with caution.(105)

Autoignition, 5 sec: 230° .(105)

Desensitization by reducing static has not been successful;
table. (117)

Desensitization: Stearic acid, humidification used to desens.(117)
By other additives.(117)

235. $C_5H_6F_8N_6O$

$CON(CH_2NF_2)CH(NF_2)CH(NF_2)N(CH_2NF_2)$

Code: BDM-BDJ (liquid)

Impact: 5-10 cm; NG = 25-30 cm; $\frac{1}{2}$ kg m.s. hammer.(243)

Thermal Stability:

DTA: No exo below 350° .(124)

VTS: Initial rate 2.9 ml/gm/100 hrs; steady rate 0.3 ml/gm/100 hrs.

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235. $C_5H_6F_8N_6O$ (continued)

(124)

Explosion point: Greater than 150° . (243)

Thermal Decomp: Initial rapid pressure rise during first 50 hrs then constant slower rate. (123)

236. $C_5H_7F_4N_5O_6$

$(O_2N)_3CCH_2CH_2C(NF_2)_2CH_3$

Code: TDFP

(solid)

Impact: 15 kg cm; RDX = 150 kg cm; Olin. (154)

Thermal Stability:

DTA: Exo at 168° ; RDX exo at 209° . (154)

Wenograd: Temp to 250 μ sec delay, 458° . (155)

237. $C_5H_8ClF_{12}N_7O_6$

$[C(NF_2)_3OCH_2-]_2CHNH_3ClO_4$

Code: FA-DHAMP

(solid)

Impact: 18 kg cm; Picatinny. (108)
3.3 cm; NOL drop height. (109)

Spark: 0.006 joules. (108)

Friction Screw: About Hardness 5. (108)

Thermal Stability:

VTS: 4.3 cc/gm/100 hrs at 90° . (105)
0.5 cc/gm/100 hrs at 60° . (108)

238. $C_5H_8F_4N_2$

$H_2C=CHCH_2CH(NF_2)CH_2NF_2$

(liquid)

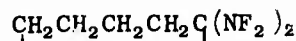
Thermal Stability:

VTS: 10.0 cc/gm/100 hrs at 90° . (93)
720 cc/mole/100 hrs at 90° . (93)

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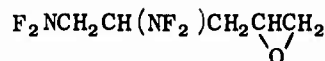
239. $C_5H_8F_4N_2$



Wenograd: Temp to 250 μ sec delay, 529°. (155)

(liquid)

240. $C_5H_8F_4N_2O$



DuPont Drop Test: 480⁺ kg cm at 50% point. (84)

Static Sens: Negative at 58,600 M.E.V. (84)

Thermal Stability:

Hot Bar: Flashed in 2 sec at 250°. (84)

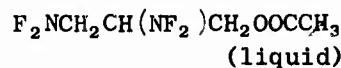
Copper Block: Fume-off at 180°. (84)

VTS: 30 cc/gm/100 hrs at 90°. (93)

5,640 cc/mole/100 hrs at 90°. (93)

(liquid)

241. $C_5H_8F_4N_2O_2$



DuPont Drop Test: Greater than 480 kg cm at 50% point. (79)

Ball Drop: Negative at 45 in with 8.3 gm ball. (79)

Static Sens: Negative at 77,500 M.E.V. (79)

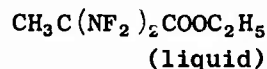
Thermal Stability:

Hot Bar: Fume-off at 250°. (79)

Copper Block: Boiled away. (79)

(liquid)

242. $C_5H_8F_4N_2O_2$



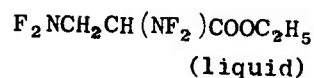
Impact: 2.8 kg in. (187)

No fire at 38 in diluted 1:1 with Freon 11. (187)

(liquid)

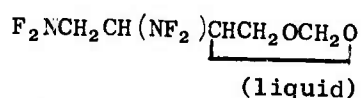
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243. $C_5H_8F_4N_2O_2$



Wenograd: Temp to 250 μ sec delay, 700°. (155)

244. $C_5H_8F_4N_2O_2$



DuPont Drop Test: 11.5 kg cm at 50% point. (79)

Ball Drop: Negative at 45 in. with 8.3 gm ball. (79)

Base Load: No. 6 lead plate. (79)

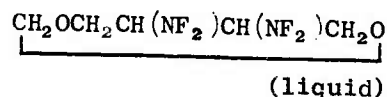
Static Sens: Negative at 77,500 M.E.V. (239)

Thermal Stability:

Copper Block: Negative at 250°. (79)

Hot Bar: Negative at 250°. (79)

245. $C_5H_8F_4N_2O_2$



DuPont Drop Test: 480⁺ kg cm at 50% point. (239)

Ball Drop: Negative at 45 in. with 8.3 gm ball. (239)

Ease Load Test: Failed. (239)

Static Sens: Negative at 77,550 M.E.V. (239)

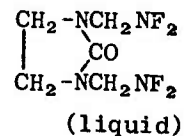
Thermal Stability:

Copper Block: Fume-off at 148° in 15 min. (239)

Hot Bar: Boil off at 250°. (239)

246. $C_5H_8F_4N_4O$

Code: BDMI



Thermal Stability:

VTS: 0.3 cc/gm/100 hrs at 60°. (125)

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247. $C_5H_8F_8N_4$

$[F_2NCH_2CH(NF_2)-]_2CH_2$
(liquid)

Code: TDP

DuPont Drop Test: 16 kg cm at 50% point. (83)

Ball Drop: Detonated at 40 in. with 8.3 gm ball. (83)

Base Load: No. 4 lead plate. (83)

Static Sens: Detonated at 10,950 M.E.V. (83)

Thermal Stability:

ETA: Minor exo at 165°; peak at 228°, boiling point. (70)

Hot Bar: Evaporation in 4 sec at 250°. (83)

Copper Block: No reaction at 250°. (83)

VTS: 0.4 cc/gm/100 hrs at 90°. (93)

110 cc/mole/100 hrs at 90°. (93)

Heat of Detonation: 1660 cal/gm; NG = 1486 cal/gm. (155)

248. $C_5H_8F_8N_4O$

$[F_2NCH_2CH(NF_2)-]_2CHOH$
(liquid)

Impact: 8 kg in. (100)

249. $C_5H_8F_8N_4O_2$

$[F_2NCH_2CH(NF_2)O-]_2CH_2$
(liquid)

Code: TDEFO

DuPont Drop Test: 11 kg cm at 50% point. (84)

Ball Drop: Detonation at 26 in. with 8.3 gm ball. (84)

Base Load Test: Failed. (84)

Static Sens: Detonation at 18,250 M.E.V. (84)

Thermal Stability:

Hot Bar: Boil-off at 250°. (84)

Copper Block: Slow fume-off at 250°. (84)

Heat of Detonation: 1510 cal/gm; NG = 1486 cal/gm. (155)

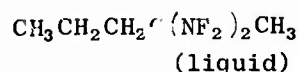
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250. $C_5H_8F_8N_6O$ $F_2NCH_2CH(NF_2)NHCONHCH(NF_2)CH_2NF_2$
Code: DEI-UREA (solid)
Impact: 180 kg cm.(45)(82)
251. $C_5H_9F_4N_3O_2$ $CH_3CH(NF_2)CH(NF_2)NHCOOCH_3$
(liquid)
Wenograd: Temp at 250 μ sec delay, 698°. (155)
252. $C_5H_9F_4N_3O_2$ $F_2NCH_2CH(NF_2)NHCOOC_2H_5$
(liquid)
Wenograd: Temp at 250 μ sec delay, 717°. (155)
253. $C_5H_{10}F_3N_3O$ $FN=N(\rightarrow O)C(CH_3)_2CH(NF_2)CH_3$
(liquid)
Thermal decomp and kinetics. (194)(242)
254. $C_5H_{10}F_4N_2$ $CH_3CH_2CH_2CH(NF_2)CH_2NF_2$
(liquid)
Thermal Stability:
VTS: 28 cc/gm/100 hrs at 23°. (95)
0.1 cc/gm/100 hrs at 90°. (94)
Effect of temp on stability, graph. (95)
In ethanol, stable at 23°, unstable at 60°. (94)
Wenograd: Temp to 250 μ sec delay, 644. (155)
Delay time to explosion vs temp., graph, table. (55)

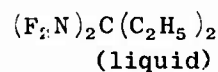
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255. $C_5H_{10}F_4N_2$



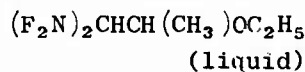
Wenograd: Temp to 250 μ sec delay, 489°. (155)
Delay time to explosion vs temp, graph, table. (55)

256. $C_5H_{10}F_4N_2$



Impact: 5.6 kg in; Picatinny. (190)

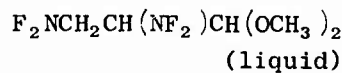
257. $C_5H_{10}F_4N_2O$



Thermal Stability:

VTS: 1.0 cc/gm/100 hrs at 110° for 145 hrs; 99.1% pure. (201)

258. $C_5H_{10}F_4N_2O_2$



DuPont Drop Test: 45 in/5 kg wt at 50% point. (79)

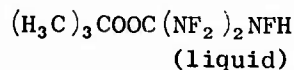
Ball Drop: Negative at 45 in with 8.3 gm ball. (79)

Static Sens: Negative at 77,500 M.E.V. (79)

Thermal Stability:

Hot Bar: Evaporated at 250°. (79)

259. $C_5H_{10}F_5N_3O_2$



Thermal Stability:

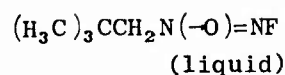
Stable for days at -78°. (143)

Slightly decomp. after 125 hrs at -21°. (145)

Decomposed less than 1 hr at 25°. (145)

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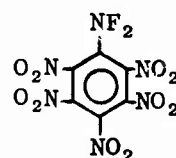
260. $C_5H_{11}FN_2O$



Thermal decomposition. (194)

261. $C_6F_2N_6O_{10}$

Code: DPNB

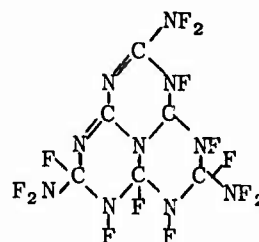


Thermal Stability:

Stable for only few minutes in atm or N_2 . (209) (solid)
Stored in solution. (209)

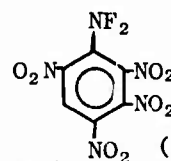
262. $C_6F_{13}N_{11}$

Impact: 3.6 kg cm. (251)



263. $C_6HF_2N_5O_8$

Code: DTNB



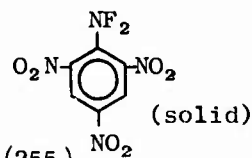
Thermal Stability:

DTA: Difference between endo and exo -96° . (209) (solid)
Endo 83; exo 179° . (209)

Stable to long storage at ambient temp. (209)

264. $C_6H_2F_2N_4O_6$

Code: FPIC



Impact: 42 cm/2 kg at 18° ; HMX = 33 cm/2 kg. (255)

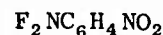
Static: 0.045 joules. (252)

Thermal Stability:

DTA: Endo 75, exo 203. (209)

Stable for long periods at ambient temp. (209)

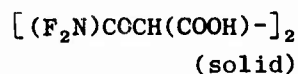
265a. $C_6H_4F_2N_2O_2$



Stable only in solution. (210)

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265b. $C_6H_4F_{12}N_6O_6$

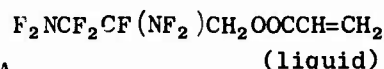


Code: FA-TA

Impact: 9.2 kg in. (284)

Friction Screw: Positive at Hardness 4. (284)

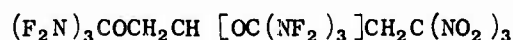
266. $C_6H_5F_7N_2O_2$



Code: NFCFPA

Impact: Greater than 38 kg in; RDX = 9.5; Picatinny. (179)

267. $C_6H_5F_{12}N_9O_8$



Code: FA-TNEEG

Impact: 10 kg cm; Picatinny. (108)

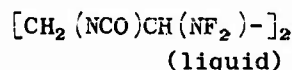
Spark: Greater than 1.8 joules. (108)

Friction Screw: Negative at Hardness 3; positive at Hardness 4. (108)

Thermal Stability:

Autoignition: 5 sec, 198°; 10 secs, 180°. (108)

268. $C_6H_6F_4N_4O_2$



Code: DBDI

Impact: Greater than 170 cm/2 kg wt at 50% point. (1)

Friction: Insensitive to initiation by friction. (1)

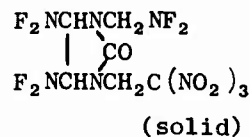
Thermal Stability:

DTA: Exo at 176°. (1)

VTS: 69 cc/gm/100 hrs at 60°. (93)

16,698 cc/mole/100 hrs at 60°. (93)

269. $C_6H_6F_6N_8O_7$



Code: BDTI

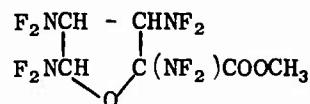
Impact: 5-10 cm; $\frac{1}{2}$ m.s. hammer. (127)

Thermal Stability:

VTS: 0.3 cc/gm/100 hrs at 60°. (127)

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270. $C_6H_6F_8N_4O_3$



Impact: ~ 1 kg in; RDX = 20 kg in. (88)

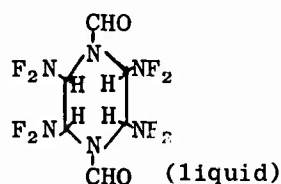
(liquid)

Thermal Stability:

Autoignition: 250° ; decomp, no explosion.

271. $C_6H_6F_8N_6O_2$

Code: DFTDP



(liquid)

Impact: 5-10 cm; NG = 25-30 cm; $\frac{1}{2}$ kg m.s. hammer. (243)

Explosion point: 202° . (243)

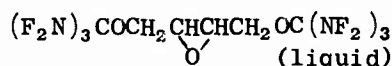
Thermal Stability:

VTS: Initial rate: 2.4 ml/gm/100 hrs. (124)

Steady rate: 0.5 ml/gm/100 hrs. (124)

Autocatalytic thermal decomp. (123)

272a. $C_6H_5F_{12}N_6O_3$



(liquid)

Code: FA-BDE

Impact: 3.5 kg in. (284)

Friction Screw: Positive with bare tools. (284)

Thermal Stability:

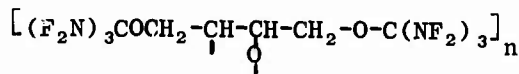
Autoignition: Table; activation energies. (115)(116)(117)

Adiabatic 250 μ sec explosions; table. (115)

Wenograd: Too sensitive to load machine. (115)

Sensitivity: Graph; table. (117)

272b. $(C_6H_5F_{12}N_6O_3)_n$



Code: Poly FA-BDE

Impact: 10 kg in. (284)

Friction Screw: Positive at Hardness 4. (284)

Thermal Stability:

Autoignition: Activation energies. (116)(117)

Thermal, solid decomposition. (64)(264)

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273. $C_6H_6F_{12}N_8O_8$

$[(F_2N)_3COCH_2CH(ONO_2)-]_2$

Code: FA-BDN

(liquid)

Impact: 5 kg cm; Esso BuMines. (105)
5 kg cm at 50% point; NG = 15 kg cm; Picatinny. (114)
0.6 kg cm at 50% point; NG = 12 kg cm; modified Picatinny. (114)
5 kg cm; Esso, Bruceton. (112)
5 kg cm; 50% point fire; Esso Picatinny. (112)
Data from different hammers; table. (113)
Variation in impact sens of neat material; table. (113)

Friction Screw: Positive with no grit; NG = Hardness 10. (114)
Test with varying tools; table; in solution, table. (113)

Spark: Greater than 1.8 joules; NG greater than 1.8 joules. (114)

Thermal Stability:

Autoignition: 5 sec, not reproducible. (105)
Table. (115)

Adiabatic 250 μ sec explosion; table. (115)

Wenograd: Too sens to load machine. (115)

Activation energy. (115)

Desensitization: Table. (114)(115)
With centralite, table; others, table. (116)
Graph: Grit hardness vs wt% FA-BDN in
halocarbon oil. (113)
Glycerin sensitizes FA-BDN; others. (113)
Addition to HPVA and alumina, table. (113)

Autoignition: Activation energy. (116)(117)

Thermal sens; graph and table. (117)

Handleability: Remote handling with difficulty. (105)

274. $C_6H_6F_{12}N_8O_8$

$[(F_2N)_3COCH_2CH(ONO_2)-]_2$

Code: Erythro FA-BDE Dinitrate

(liquid)

Impact: 16 kg cm. (103)

Friction: Doesn't detonate; 20 mesh glass in Wig-L-Bug. (103)

Spark: Greater than 0.43 joules. (103)

Thermal Stability:

DTA: Exo maximum at 172°. (103)

VTS: 0.7 cc/gm/100 hrs at 60°. (103)

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275. $C_6H_6F_{12}N_8O_8$

$[(F_2N)_3COCH_2CH(ONO_2)-]_2$
(liquid)

Code: Threo FA-BDE Dinitrate

Impact: 5 kg cm. (103)

Friction: Detonated; 20 mesh glass in Wig-L-Bug. (103)

Spark: Greater than 0.43 joules. (103)

Thermal Stability:

DTA: Exo maximum at 178° . (103)

276. $C_6H_6F_{18}N_9O_4P$

$O=P[-CH_2OC(NF_2)_3]_3$
(solid)

Code: FA-PO

Impact: Less than 3 kg cm for 5 mm needles; 10 kg cm for fine powder. (102)

Spark: Less than or equal to 0.004 joules to explosion. (102)

Thermal Stability:

DTA: Exo at 225° . (101)

Autoignition, 5 sec: 219° . (102)

VTB: 6.7, 2.0 cc/gm/100 hrs at 60° . (102)

277. $C_6H_7F_4N_3O_2$

$F_2NCH_2CH(NF_2)CH(CN)OOCCH_3$
(liquid)

DuPont Drop Test: Greater than 480 kg cm at 50% point. (79)

Base Load Test: No. 6 lead plate. (79)

Static Sens: Negative at 77,500 M.E.V. (79)

278. $C_6H_7F_6N_3O_2$

$CH_2=CHCOOCH_2C(NF_2)_2CH_2NF_2$
(liquid)

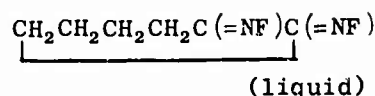
Code: TNFPA

DTA: Exo at 258° . (195)

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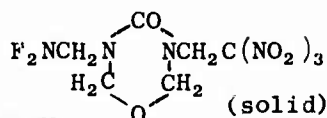
CONFIDENTIAL

279. $C_6H_8F_2N_2$



Decomposition at 80° in VPC apparatus. (230)

280. $C_6H_8F_2N_6O_8$



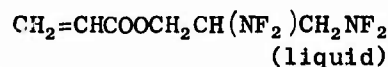
Code: DT-URON

Explosion point: 153° . (127)

Thermal Stability:

VTS: 4.7 cc/gm/100 hrs at 60° . (125)

281. $C_6H_8F_4N_2O_2$



Code: NFFA

Impact: Greater than 100 cm/2 kg wt; mod BuMines. (20)

Greater than 635 kg cm. (68)

96 kg cm. (45)

5 kg cm/1 kg wt at 50% point; n-propylnitrate = 8 cm;
Olin. (239)

Greater than 38 kg in. at 50% point; NG = 10.7 kg in; Picatinny. (198)

DuPont Drop Test: Greater than 56 in/5 kg wt at 50% point. (79)

Card Gap: 1.21 in; NG = 0.91 in. (198)

Static Sens: Greater than 77,500 M.E.V. (79)

Negative at 1 joule; positive at 2 joules. (198)

Negative at 0.50 joules; positive at 1.00 joules. (27)

Friction: Negative at 7000 rpm; Aerojet rotational friction machine. (20)

Thermal Stability:

DTA: Exo peak, 225° , preceded by polymerization peak; NG = 196° . (198)

Copper Block: 182° at 8 min 12 sec. (79)

VTS: No gas evolution/40 hrs at 90° and 200 mm pressure. (239)

Pressure rise vs time, table. (27)

Desensitization. (20)

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282. $C_6H_8F_4N_2O_2$ $F_2NCH_2CH(NF_2)OOC(CH_3)=CH_2$
Code: NFEMA (liquid)

Impact: Greater than 38 kg in; RDX = 9.5; Picatinny. (179)

283. $C_6H_8F_4N_2O_4$ $[HCOOCH_2CH(NF_2)-]_2$
(liquid)

Impact: 480^+ kg cm; modified DuPont. (85)

Base Load Test: No. 1 lead plate. (85)

Thermal Stability:

Hot Bar: Fumed-off at 250° . (85)

Copper Block: Decomposed after 7-10 min with temp of $190-230^\circ$. (85)

284. $C_6H_8F_6N_6O_{10}$ $(F_2N)_3COCH_2C(CH_2ONO_2)_3$
Code: FA-PETRIN (liquid)

Impact: 11.5 kg cm; Picatinny. (109)
2.0 kg cm; NG = 10.0 kg cm.; Bruceton. (111)

Spark: Greater than 1.8 joules. (109)

Friction Screw: Hardness 4. (109)

Thermal Stability:

DTA: Exo at 207° . (108)

VTS: Less than 0.1 cc/gm/100 hrs at 60° . (109)
0.50 cc/gm/100 hrs at 75° . (109)
4.5-5.6 cc/gm/100 hrs at 90° . (109)

285. $C_6H_8F_8N_4$ $F_2NCH_2CH(NF_2)CH=CHCH(NF_2)CH_2NF_2$
(liquid)

VTS: 2.0 cc/gm/100 hrs at 90° . (94)

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286. $C_6H_8F_8N_4$

Code: TDC $\overline{CH_2CH_2C(NF_2)_2CH_2CH_2C(NF_2)_2}$ (liquid)

Impact: 5-10 cm; $\frac{1}{2}$ kg m.s. hammer.(127)
5 kg cm.(45)

Explosion point: Decomp. without explosion at 266° .(127)

287. $C_6H_8F_8N_4O_2$

$F_2NCH_2CH(NF_2)CH(NF_2)CH(NF_2)OOCCH_3$
(liquid)

DuPont Drop Test: 60 kg cm at 50% point.(84)

Ball Drop: Negative at 45 in with 8.3 gm ball. (84)

Base Load Test: No. 5 lead plate.(84)

Static Sens: Detonated at 13,700 M.E.V.(84)

Thermal Stability:

Hot Bar: Evaporation after 1 sec at 250° . (84)

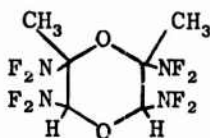
Copper Block: No reaction at 250° .(84)

288. $C_6H_8F_8N_4O_2$

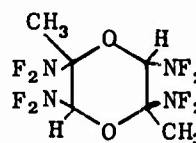
$CH_3CH(NF_2)CH(NF_2)COOCH(NF_2)CH_2NF_2$
(liquid)

Heat of detonation: 1360 cal/gm; NG = 1486 cal/gm.(155)

289. $C_6H_8F_8N_4O_2$



or



(liquid)

Impact: 5-10 cm; $\frac{1}{2}$ kg m.s. hammer.(127)

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290. $C_6H_8F_8N_6O_6$ $[F_2NCH_2CH(NF_2)CHCONO_2]_2$
(liquid)

DuPont Drop Test: Detonated at 15 kg cm at 50% point. (239)

Ball Drop: Negative at 45 in. with 8.3 gm ball. (239)

Static Sens: Negative at 77,500 M.E.V. (239)

Thermal Stability:

Copper Block: Fume-off at 140°; violent decomp at 155°. (239)

Hot Bar: Flashed at 250°. (239)

291. $C_6H_8F_8N_6O_6$ $[F_2NCH_2CH(NF_2)CH(ONO_2)]_2$
Code: TDHD (solid)

Ball Drop Test: Detonated at 1 in with 8.3 gm ball. (70)

Base Load Test: No. 1 lead plate. (70)

Static Sens: Detonated at 0.0072 joule. (70)

Thermal Stability:

DTA: Endo at 81°; decomp start at 90° with major peak at 160°. (85)

Copper Block: Fumed-off at 160-170° in 5.5 min. (70)

Hot Bar: Flashed and shot instantly at 250°. (70)

9 mg exploded during fluorine analysis. (85)

292. $C_6H_8F_8N_6O_6$ $[F_2NCH_2CH(NF_2)CH(ONO_2)]_2$
Code: TDHD (liquid)

DuPont Drop Test: 6 kg cm at 50% point. (70)

5 kg cm at minimum positive fire. (70)

Base Load Test: No. 1 lead plate. (70)

Static Sens: Detonated at 0.262 joule. (70)

Thermal Stability:

DTA: Exo at 171° and 164°. (70)

Copper Block: No reaction at 250° for 15 min. (70)

Hot Bar: Instant detonation at 250°. (70)

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293. $C_6H_8F_{12}N_6$

$[F_2NCH_2CH(NF_2)CH(NF_2)-]_2$

Code: HDH

(liquid)

Impact: 106 cm/2 kg wt at 50% point; modified BuMines.(1)

Thermal Stability:

DTA: Endo at 178°.(1)

VTS: 2.6 cc/gm/100 hrs at 90°.(94)

294a. $C_6H_8F_{12}N_6O$

$[F_2NCH_2CH(NF_2)CH(NF_2)-]_2O$

Code: HFE

(liquid)

Impact: 2-4 cm/2 kg at 50% point; NG = > 100 cm/2 kg at 50% point;
mod BuMines.(20)

9.5 kg cm; mod DuPont tester.(75)

2.3 kg cm; NG = 10.0 kg cm; Bruceton.(111)

5 kg cm at 50% point; Esso Picatinny.(112)

2.5 kg cm.(232)

Base Load: No. 0 lead plate.(75)

Card Gap: 1.19 in; nitroglycerin = 0.91 in.(198)

Friction Sens: Negative at 1000 rpm; positive at 1600 rpm.(232)

Friction Screw Test: Detonated with glass.(105)

Hardness 5.5 (116)

Wig-L-Bug Friction: Negative. (103)

Static: Negative at 0.01 joules; positive at 0.05 joules.(232)

Negative.(75)

Greater than 0.43 joules.(105)

Thermal Stability:

DTA: Endo at 263°.(20)

Exo at 232°.(70)

Exo maximum at 255°.(103)

Exo at 230°.(195)

Slight exo at 203°-208°, large endo at 210°-230°.(232)

Copper Block: No reaction to 250°.(75)

Hot Bar: No ignition at 250°.(74)

Autoignition, 5 sec: 369°.(105)

VTS: When treated in various ways, gas evolved/gm/100 hrs
at 27° varied from sev. cc to 0.12 cc.(101)

0.12 cc/gm/100 hrs at 40°.(102)

0.0 cc/gm/100 hrs at 60°.(103)

1.0 cc/gm/100 hrs at 90°.(104)

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294a. $C_6H_8F_{12}N_6$ (continued)

Significant degradation occurred on extended storage of
HPE in 10% solution in Freon 113. (103)

Remote handling without difficulty. (105)

Desensitization: Of friction with various additives. (112)

Autoignition: Activation energies. (116)(117)

Thermal sens, graph, table. (117)

Thermal stability at 65°, table. (20)

Decomposition Studies: Rate of HF elimination in aqueous solution. (103)

294b. $C_6H_8F_{12}N_6O_2$

Code: FABD

$[(F_2N)_3COCH_2CH_2-]_2$
(liquid)

Impact: 6 kg cm. (284)

295. $C_6H_8F_{12}N_6O_4$

Code: FA-BDG

$[(F_2N)_3COCH_2CH(OH)-]_2$
(solid)

Thermal Stability:

Graph, table. (117)

Autoignition: Activation energy. (116)(117)

296. $C_6H_8F_{12}N_8O_4$

Code: FA-DENA

$[(F_2N)_3COCH_2CH_2-]_2NNO_2$

Thermal Stability:

VTS: Off scale after 15 hrs at 60°. (110)

297. $C_6H_9F_4N_3O_2$

Code: C₄PFG

$FN-C(NF_2)[NFCOO(CH_2)_3CH_3]$
(liquid)

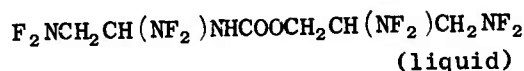
Thermal Stability:

DTA: Endo at 178°, exo at 181°. (17)

Storable for sev. wks without decomp. (17)

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298. $C_6H_9F_8N_5O_2$



DuPont Drop Test: Positive at 48 in/5 kg wt at 50% point. (79)

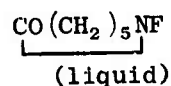
Static Sens: Negative at 77,500 M.E.V. (79)

Thermal Stability:

Hot Bar: Fume-off at 250° . (79)

Wenograd: Temp at 250 μ sec delay, 566° . (155)

299. $C_6H_{10}FNO$

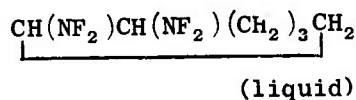


Impact: Not sensitive. (8)

Thermal Stability:

DTA: Exo at 184° . (8)

300. $C_6H_{10}F_4N_2$



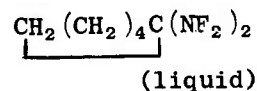
Impact: Insensitive. (230)

Thermal Stability:

Wenograd: Temp to 250 μ sec delay, 654° . (155)

Delay time to explosion vs temp; graph, table. (55)

301. $C_5H_{10}F_4N_2$

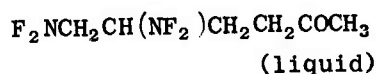


Thermal Stability:

Wenograd: Temp to 250 μ sec delay, 529° . (155)

Delay time to explosion vs temp; graph, table. (55)

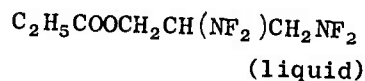
302. $C_6H_{10}F_4N_2O$



Wenograd: Temp to 250 μ sec delay, 686° . (155)

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303. $C_6H_{10}F_4N_2O_2$



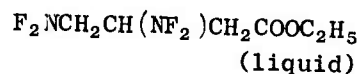
Code: APA

Thermal Stability:

DTA: 185° endo, at b.p.; NG = 196.(198)

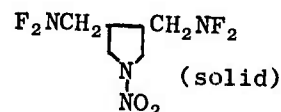
Wenograd: Temp at 250 μ sec delay, 702° .(155)

304. $C_6H_{10}F_4N_2O_2$



Wenograd: Temp to 250 μ sec delay, 704° .(155)

305. $C_6H_{10}F_4N_4O_2$

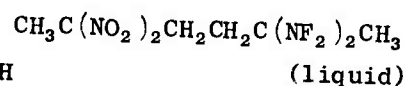


Thermal Stability:

VTS: No gas evolution after 2 wks at 90° .(95)

DTA: Endo at melting point, 55° ; exo begins at 100° ,
deflagration at 180° .(95)

306. $C_6H_{10}F_4N_4O_4$



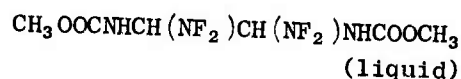
Code: DDFH

Impact: Greater than 80 kg cm; RDX = 150 kg cm; Olin.(154)

Thermal Stability:

DTA: Exo at 202° ; RDX exo at 209° .(154)

307. $C_6H_{10}F_4N_4O_4$

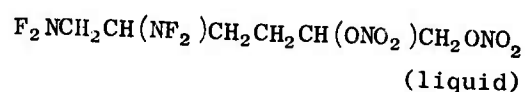


Thermal Stability:

Storable in dry glassware.(92)

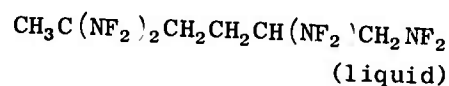
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308. $C_6H_{10}F_4N_4O_6$



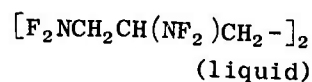
Impact: 22 kg in; Picatinny.(188)

309. $C_6H_{10}F_8N_4$



Extremely shock sensitive.(237)

310. $C_6H_{10}F_8N_4$



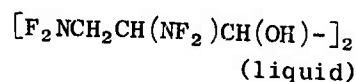
Code: TDH
TNFH

Impact: 1 kg cm.(45)

Thermal Stability:

DTA. Start minor activity at 139° , peak at 228° .(70)
Exo peak at 205° , endo at b.p.; NG exo at 196° .(198)

311. $C_6H_{10}F_8N_4O_2$



DuPont Drop Test: Negative at 56 in/2 kg wt at 50% point. (79)

Ball Drop: Negative at 45 in. with 8.3 gm ball.(79)

Static Sens: Negative at 77,500 M.E.V.(79)

Base Load Test: No. 6 lead plate.(79)

Thermal Stability:

Copper Block: Fume-off at 125° .(79)

Hot Bar: Flashed at 250° .(79)

VTS: 60 cc/gm/100 hrs at 60° .(93)

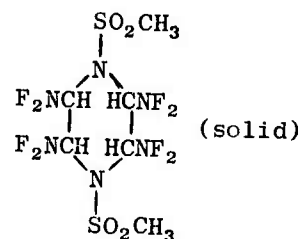
19,320 cc/mole/100 hrs at 60° .(93)

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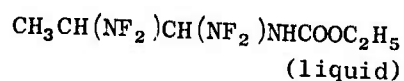
312. $C_6H_{10}F_8N_6O_4S_2$

Impact: 20-40 cm; $\frac{1}{2}$ kg m.s. hammer. (127)

Explosion Point: Greater than 250° . (127)

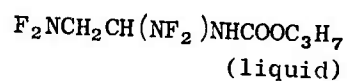


313. $C_6H_{11}F_4N_3O_2$



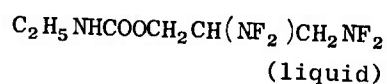
Wenograd: Temp at 250 μ sec delay, 695° . (155)

314. $C_6H_{11}F_4N_3O_2$



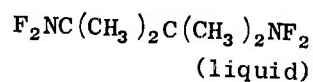
Wenograd: Temp at 250 μ sec delay, 717° . (155)

315. $C_6H_{11}F_4N_3O_2$



Wenograd: Temp at 250 μ sec delay, 623° . (155)

316. $C_6H_{12}F_4N_2$

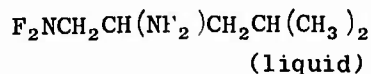


Thermal Stability:

VTS: 0.4 cc/gm/100 hrs at 90° . (94)

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317. $C_6H_{12}F_4N_2$



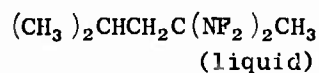
Impact: 10.1 kg cm at 50% point; Olin. (178)

Thermal Stability:

Wenograd: Temp to 250 μ sec delay, 502°. (155)

Delay time to explosion vs temp; graph, table. (55)

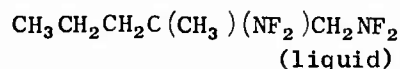
318. $C_6H_{12}F_4N_2$



Decomposition. (59)

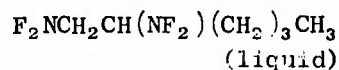
Decomposition Kinetics, solution. (59)

319. $C_6H_{12}F_4N_2$



Impact: 31.2 kg in. at 50% point. (175)

320. $C_6H_{12}F_4N_2$

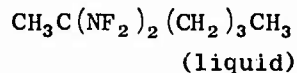


Thermal Stability:

Wenograd: Temp to 250 μ sec delay, 765°. (155)

Delay time to explosion vs temp; graph, table. (55)

321. $C_6H_{12}F_4N_2$



Impact: Sensitive.

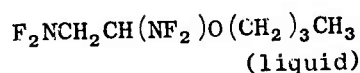
Thermal Stability:

Wenograd: Temp to 250 μ sec delay, 502°.

Delay time to explosion vs temp; graph, table. (55)

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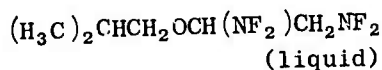
322. $C_6H_{12}F_4N_2O$



Thermal Stability:

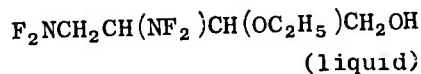
VTS: 0.015 cc/gm/100 hrs at 60°; 95% pure. (201)
0.16 cc/gm/100 hrs at 80°; 95% pure. (201)
0.60 cc/gm/100 hrs at 100°; 95% pure. (201)

323. $C_6H_{12}F_4N_2O$



No gas evolved at 50° and 100° for 648 hrs each. (202)

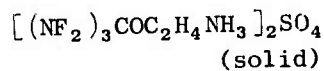
324. $C_6H_{12}F_4N_2O_2$



Thermal Stability:

VTS: 1.3 cc/gm/100 hrs at 60° for 645 hrs. (202)
10.2 cc/gm/100 hrs at 80° for 216 hrs. (202)
194 cc/gm/100 hrs at 100° for 34-36 hrs. (202)

324 a. $C_6H_{14}F_{12}N_8O_6S$



Code: INFO-1266 S

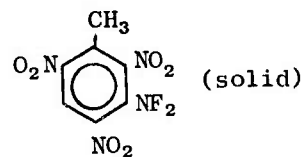
Impact: 6.0 cm; NOL drop height. (146)

325. $C_7H_4F_2N_4O_6$

Thermal Stability:

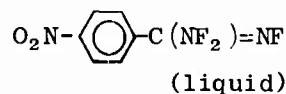
DTA: Endo at 112°; exo at 195°. (209)

Stable to long storage at ambient temp and moisture. (209)



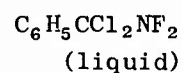
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326. $C_7H_4F_3N_3O_2$



Impact: 2 of 2 tries fired at 32.4 in; 0 of 2 tries fired at 22.8 in. (182)

327. $C_7H_5Cl_2F_2N$

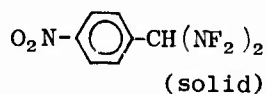


Impact: Greater than 90 cm / 2 kg; RDX = 26 cm / 2 kg. (15)

Thermal Stability:

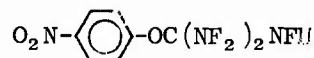
DTA: Endo at 216° . (15)

328. $C_7H_5F_4N_3O_2$



Impact: 2 of 2 tries fired at 5.6 in; 0 of 2 tries fired at 4.0 in. (183)

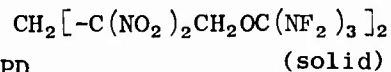
329. $C_7H_5F_5N_4O_3$



Thermal Stability:

Relatively stable; slight decomp after 15 days at 25° . (245)

330a. $C_7H_6F_{12}N_{10}O_{10}$



Code: FA-TNPD

Impact: 25 kg cm : Picatinny. (105)

Spark: Greater than 0.96 joules. (105)

Friction: Detonates with glass. (105)

Wig-L-Bug Friction: Negative. (103)

Thermal Stability:

DTA: Exo maximum at 172° ; endo at 68° . (103)

VTS: 2.0 cc/gm/100 hrs at 60° . (105)

8.0, 11.0 cc/gm/100 hrs at 80° for 10 hrs. (105)

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330b. $C_7H_6F_{16}N_8O_2$ $[(F_2N)_3CNHCOCH_2-]_2C(NF_2)_2$
(solid)

Code: BPBTC

Impact: 28 kg cm. (284)

331. $C_7H_6F_{16}N_{10}O_4$ $(F_2N)_2C[CH_2OOCNHC(NF_2)_3]_2$
(liquid)

Impact: 11 kg in. (98)

Thermal Stability:

VTS: 3.5 cc/142 hrs at 60°. (98)

DTA: Endo at 92.5°; exo at 129° (small), 178° (broad). (98)

332. $C_7H_6F_{18}N_{10}O_5$ $[(F_2N)_3COCH_2-]_3CNO_2$
(solid)

Code: FA-NG

Impact: 5 kg cm. (102) (284)
2 kg in. (99)

Spark: 0.79 joules to explosion. (102)

Thermal Stability:

DTA: Slow decomp from 195°; exo at 225°. (99)

Autoignition, 5 sec: 234°. (102)

VTS: 1.0 cc/gm/100 hrs at 60°. (102)
4.0 cc/gm/100 hrs at 90°. (102)

333. $C_7H_6F_{20}N_{10}O_3$ $[(F_2N)_3COCH_2]_3CNF_2$
(liquid)

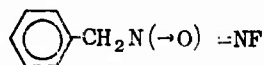
Code: FA-BDAT

Thermal Stability:

DTA: Exo start at 200°, complete at 250°. (103)

VTS: 0.9 cc/gm/100 hrs at 60°. (103)

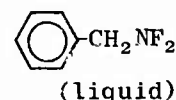
334. $C_7H_7FN_2O$



Thermal decomposition. (194)

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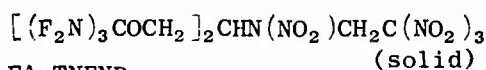
335. $C_7H_7F_2N$



Thermal Stability:

VTS: 18.4 cc/gm/100 hrs at 90°. (93)
2631 cc/mole/100 hrs at 90°. (93)

336. $C_7H_7F_{12}N_{11}O_{10}$



Code: FA-TNEND

Impact: 13 kg cm; Picatinny. (109)

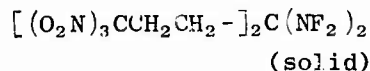
Spark: 0.01-0.03 joules. (109)

Friction Screw: Hardness 4. (109)

Thermal Stability:

VTS: 0.25-0.35 cc/gm/100 hrs at 60°. (109)
1.4 cc/gm/100 hrs at 75°. (109)
9.2 cc/gm/74 hrs at 90°

337. $C_7H_8F_4N_8O_{12}$



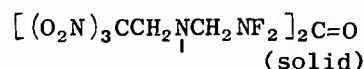
Code: HDFH

Impact: 125 kg cm; RDX = 150 kg cm; Olin. (154)

Thermal Stability:

DTA: Exo at 150°; RDX exo at 209°. (154)

338. $C_7H_8F_4N_{10}O_{13}$



Code: BDBTU

Impact: 5-10 cm; $\frac{1}{2}$ kg m.s. hammer. (127)

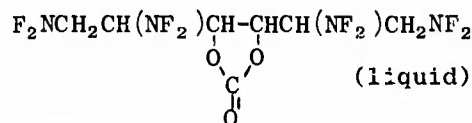
Explosion Point: 169°. (127)

Thermal Stability:

VTS: 0.5 cc/gm/100 hrs at 60°. (127)

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339a. $C_7H_8F_8N_4O_3$



DuPont Drop Test: Greater than 480 kg cm
at 50% point. (79)

Ball Drop: Negative at 45 in with 8.3 gm ball. (79)

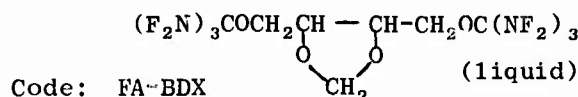
Static Sens: Negative at 77,500 M.E.V. (79)

Thermal Stability:

Copper Block: Fume-off at 155°. (79)

Hot Bar: Flashed at 250°. (79)

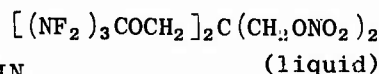
339b. $C_7H_8F_{12}N_6O_3$



Code: FA-BDX

Friction Screw: Positive at Hardness 5.5. (284)

340. $C_7H_8F_{12}N_8O_8$



Code: FA-PEDIN

Impact: 2.3 kg cm; Bruceton. (109)
5.5 kg cm; Picatinny. (109)

Spark: Greater than 1.8 joules. (109)

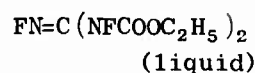
Friction Screw: Hardness 4. (109)

Thermal Stability:

VTS: 0.7-1.1 cc/gm/100 hrs at 60°. (109)
4.3 cc/gm/65 hrs at 75°. (109)
19.3 cc/gm/100 hrs at 90°. (109)

Decomposition is autocatalyzed above 75°. (109)

341. $C_7H_{10}F_3N_3O_4$



Code: DC2PFG

Impact: 4 cm/2 kg at 0% point; 4.5 cm/2 kg at 50% point; 5.0 cm/2 kg
at 100% point; Olin. (17)

Thermal Stability:

Storable for sev.wks without decomp. (17)

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342. $C_7H_{10}F_4N_2O_2$ $F_2NCH_2C(NF_2)(CH_3)CH_2OOCCH=CH_2$
Code: NFIBA (liquid)
Impact: Greater than 38 kg in; RDX = 9.5 kg in; Picatinny.(179)

343. $C_7H_{10}F_4N_2O_2$ $F_2NCH_2CH(NF_2)CH_2OOC(CH_3)=CH_2$
Code: NFPMA (liquid)
Impact: Greater than 38 kg in; RDX = 9.5 kg in; Picatinny.(179)
Thermal Stability:
DTA: Exo at 191°. (197)

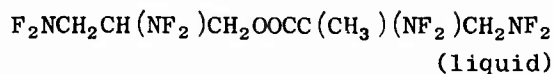
344. $C_7H_{10}F_4N_2O_4$ $F_2NCH_2CH(NF_2)CH(OOCCH_3)_2$
(liquid)
DuPont Drop Test: Negative at 56 in/5 kg v.)
Ball Drop: Negative at 45 in with 8.3 gm ball.(79)
Static Sens: Negative at 77,500 M.E.V. (79)
Thermal Stability:
Hot Bar: Instantly evaporated at 250°. (79)

345. $C_7H_{10}F_4N_2O_4$ $H_3CCOOCH_2C(NF_2)(OOCCH_3)CH_2NF_2$
(liquid)
Impact: Insensitive.(195)

346. $C_7H_{10}F_8N_4O_2$ $F_2NCH_2CH(NF_2)CH_2COOCH(NF_2)CH(NF_2)CH_3$
Code: TAVA (liquid)
DuPont Drop Test: 390 kg cm; minimum positive fire.(74)
Static Sens: Not sensitive. (75)
Thermal Stability:
DTA: Start decomp at 140°; major exo at 250°. (75)
Copper Block: Ignites at 245°. (75)
Hot Bar: No ignition at 250°. (74)

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347. $C_7H_{10}F_8N_4O_2$



DuPont Drop Test: 13.5 kg cm at 50% point.(79)

Ball Drop: Negative at 45 in with 8.3 gm ball.(79)

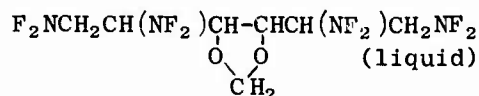
Static Sens: Negative at 77,500 M.E.V.(79)

Thermal Stability:

Copper Block: Boiled and fumed-off.(79)

Hot Bar: Boiled and fumed-off at 250°.(79)

348. $C_7H_{10}F_8N_4O_2$



Code: BBDED

Impact: 13 kg cm.(71)

DuPont Drop Test: 11.5 kg cm at 50% point.(79)

Ball Drop: Negative at 45 in with 8.3 gm ball.(79)

Base Load: No. 6 lead plate.(79)

Static Sens: Negative at 77,500 M.E.V. (239)

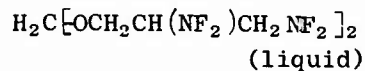
Thermal Stability:

Copper Block: Boil-off at 250°.(79)

Hot Bar: Fume-off at 250°.(79)

Stable upon storage.(71)

349. $C_7H_{12}F_8N_4O_2$



DuPont Drop Test: 18 kg cm at 50% point.(239)

Ball Drop: Negative at 45 in with 8.3 gm ball.(239)

Static Sens: Negative at 77,500 M.E.V. (239)

Thermal Stability:

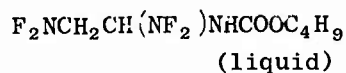
Copper Block: Slow fume-off at 250° in 15 min. (239)

Hot Bar: Fume-off at 250° in 3 sec.(239)

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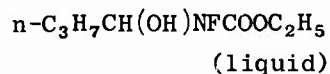
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350. $C_7H_{13}F_4N_3O_2$



Wenograd: Temp at 250 μ sec delay, 729°. (155)

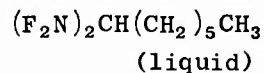
351. $C_7H_{14}FNO_3$



Thermal Stability:

Unstable, dissociates to starting material. (7)

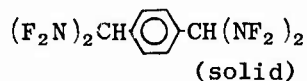
352. $C_7H_{14}F_4N_2$



Code: BDH

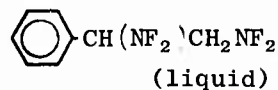
DTA: Endo at 170°, boiling point. (71)

353. $C_8H_6F_8N_4$



Impact: 1 of 1 try fired at 2.8 in; 1 of 3 tries fired at 1.9 in. (183)

354. $C_8H_8F_4N_2$



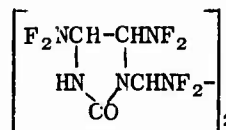
Thermal Stability:

VTS: 15.3 cc/gm/100 hrs at 90°. (93)
2188 cc/mole/100 hrs at 90°. (93)

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355. $C_8H_8F_{12}N_{10}O_2$

Code: HHBIE



Impact: 5-10 cm; $\frac{1}{2}$ kg m.s. hammer. (127)

(solid)

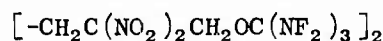
Explosion Point: 163-166°. (127)

Thermal Stability:

VTS: Initial rate - 1.5 cc/gm/100 hrs at 60°. (124)

Steady rate - 0.3 cc/gm/100 hrs at 60°. (124)

356. $C_8H_8F_{12}N_{10}O_{10}$



Code: FA-TNH

(solid)

Impact: 5.3 kg cm; Bruceton. (110)

8.5 kg cm; Picatinny. (284)

Spark: Greater than 1.8 joules. (110)

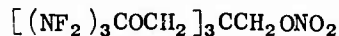
Friction: Negative at Hardness 3; positive at Hardness 4. (110)

Thermal Stability:

VTS: 0.2-0.35 cc/gm/600 hrs at 60°. (110)

1.5 cc/gm/600 hrs at 90°. (110)

357. $C_8H_8F_{18}N_{10}O_6$



Code: FA-PEMON

(liquid)

Impact: 2.9-4.3 kg cm; Bruceton. (109)

0.9 kg cm; NG = 10.0 kg cm; Bruceton. (111)

Spark: Greater than 1.8 joule. (109)

Friction: Hardness 4. (117)

Thermal Stability:

VTS: 0.7-1.1 cc/gm/100 hrs at 60°. (109)

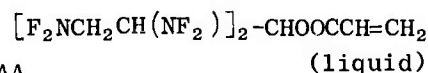
3.2 cc/gm/100 hrs at 75° for 70 hrs. (109)

2.2 cc/gm/100 hrs at 90° for 30 hrs. (109)

Activation energy: 37.209 kcal/molc, autoignition. (117)

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358. $C_8H_{10}F_8N_4O_2$



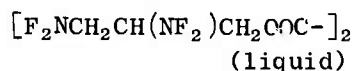
Code: TAA

Impact: 8 kg in; Picatinny.(100)

Thermal Stability:

VIS: 2.0, 0.8 cc/gm/100 hrs at 60°. (99)

359. $C_8H_{10}F_8N_4O_4$



DuPont Drop Test: 135 kg cm at 50% point.(79)

Ball Drop: Negative at 45 in with 8.3 gm ball.(79)

Base Load: No. 5 lead plate.(79)

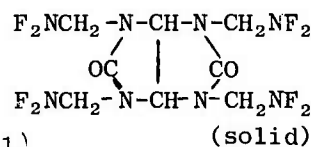
Static Sens: Negative at 77,500 M.E.V.(79)

Thermal Stability:

Copper Block: Fume-off at 230° in 14 min 57 sec.(79)

Hot Bar: Boiled and fume away at 250°. (79)

360. $C_8H_{10}F_8N_8O_2$

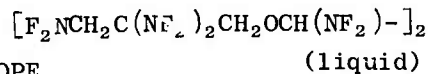


Impact: 10-20 cm; $\frac{1}{2}$ kg m.s. hammer. (121)

Thermal Stability:

Explosion Point: 234°. (121)

361. $C_8H_{10}F_{16}N_8O_2$



Code: OPE

Impact: 4 kg in at 100% point; RDX = 10.2; Picatinny.(199)

2.5 kg in at 50% point: RDX = 10.2; Picatinny.(199)

5.3 cm/2 kg wt at 50% point.(28)

Friction: Negative at 500 rpm for 120 sec; positive at 600 rpm for 90 sec.(199)

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361. $C_8H_{10}F_{16}N_8O_2$ (continued)

Static Sens: No reaction at limit of test. (199)
0.13 joules at 50% point. (28)

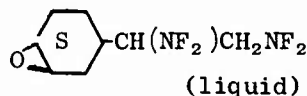
Card Gap: 1.03 in; NG = 0.91 in. (198)

Thermal Stability:

DTA: Doublet at 238 and 260°. (199)
Exo at 185°, 213°. (28)

VTS at 65°, chart. (28)

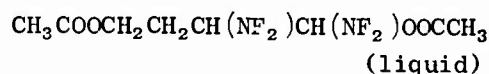
362. $C_8H_{12}F_4N_2O$



Thermal Stability:

VTS: 7 cc/gm/100 hrs at 90°. (93)
1596 cc/mole/100 hrs at 90°. (93)

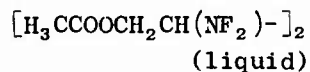
363. $C_8H_{12}F_4N_2O_4$



Thermal Stability:

VTS: 0.5 cc/gm/100 hrs at 90°. (93)
148 cc/mole/100 hrs at 90°. (93)

364. $C_8H_{12}F_4N_2O_4$



DuPont Drop Test: Greater than 480 kg cm at 50% point. (81)

Ball Drop: Negative at 45 in with 8.3 gm ball. (81)

Base Load: No. 6 lead plate. (81)

Static Sens: Negative at 77,500 M.E.V. (81)

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364. $C_8H_{12}F_4N_2O_4$ (continued)

Thermal Stability:

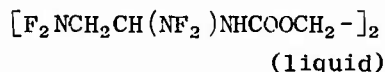
Copper Block: Slow fume-off after 15 min at 250° . (81)

Hot Bar: Fume-off at 250° . (81)

Gas Evolution: No cc/gm/100 hrs at 80° for 2950 hrs; $\sim 95\%$ pure. (201)
13.6 cc/gm/100 hrs at 120° for 71.5 hrs;
 $\sim 95\%$ pure. (201)

No decomp upon distillation at 100° . (90)

365. $C_8H_{12}F_8N_6O_4$



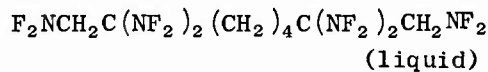
DuPont Drop Test: Negative at 56 in/2 kg wt at 50% point. (79)

Static Sens: Negative at 77,500 M.E.V. (79)

Thermal Stability:

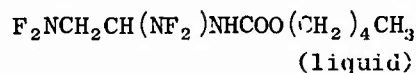
Wenograd: Temp at 250 μ sec delay, 635° . (155)

366. $C_8H_{12}F_{12}N_6$



Impact: 5-6 kg in; RDX = 10 kg in; Picatinny. (184)

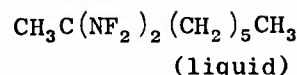
367. $C_8H_{15}F_4N_3O_2$



Wenograd: Temp at 250 μ sec delay, 789° . (155)

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368. $C_8H_{16}F_4N_2$

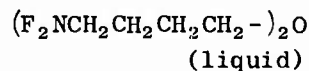


Impact: 50% on glass cloth - 20 cm/2 kg wt. (8)
100% on glass cloth - 23 cm/2 kg wt. (8)
0% on glass cloth - 17 cm/2 kg wt. (8)

Spark Sens: Negative at 2.5 joules; partially positive at 4.5 joules; positive at 40 joules. (8)

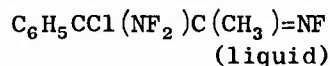
Friction Sens: Negative at 3000 rpm/2 kg for 2 min, but positive at 3500 rpm/2 kg for 0.52 min. (8)

369. $C_8H_6F_4N_2O$



Impact: Greater than 38 kg in. (190)

369a. $C_9H_8ClF_3N_2$

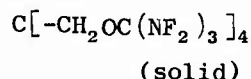


Code: PNFP

DTA: Exo at 230°, decomp. (197)

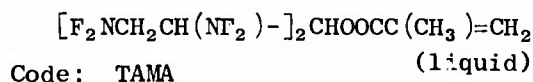
370. $C_9H_8F_{24}N_{12}O_4$

Code: FA-PE



Impact: Less than 1 kg cm; Picatinny. (107)

371. $C_9H_{12}F_8N_4O_2$



Impact: 42 cm/2 kg wt. (27)

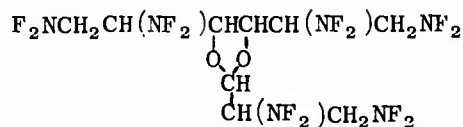
Spark: Negative at 0.25 joules; positive at 0.50 joules. (27)

Thermal Stability:

VTS: Stability at 65°, table. (27)

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372. $C_9H_{12}F_{12}N_6O_2$



DuPont Drop Test: 22.5 kg cm at 50% point. (79) (liquid)

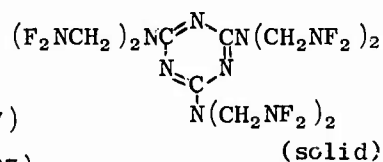
Static Sens: Negative at 77,500 M.E.V. (79)

Thermal Stability:

Copper Block: Fume-off at 250° . (79)

Hot Bar: Slow fume-off at 250° . (79)

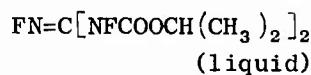
373. $C_9H_{12}F_{12}N_{12}$



Impact: 5-10 cm; $\frac{1}{2}$ kg m.s. hammer. (127)

Explosion Point: Greater than 260° . (127)

374. $C_9H_{14}F_3N_3O_4$



Code: DC₃₁ PFG

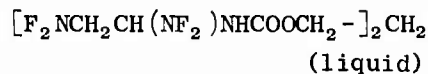
Impact: 3 cm/2 kg at 50% point; Olin. (17)

Thermal Stability:

DTA: Exo at 223° . (17)

Storable for sev. wks without decomp. (17)

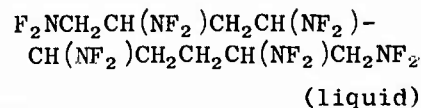
375. $C_9H_{14}F_8N_6O_4$



Wenograd: Temp at 250 μ sec delay, 620° . (155)

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376. $C_9H_{14}F_{12}N_6$

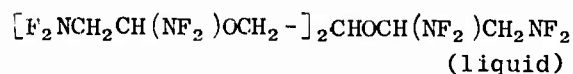


Code: HDN

Thermal Stability:

DTA: Exo peak at 211° ; NG = 196° . (198)

377. $C_9H_{14}F_{12}N_6O_3$



Code: TVOPA

Impact: 2-3 cm/2 kg at 50% point; BuMines. (20)

129 kg cm. (75)

8 kg in; RDX = 10.8 kg in. (174)

10 kg cm; NG = 10.0 kg cm; Bruceton. (111)

11 kg in; NG = 11 kg in; Picatinny. (191)

4.0 kg cm. (232)

Bottle Drop Height: 10 ft. (198)

Base Load: No. 0 lead plate. (75)

Friction Sens: Positive at 0.37 relative friction no. at 750 rpm. (20)

Negative at -2700 rpm; positive at 2800 rpm. (232)

Static Sens: Negative. (75)

Negative, 1 joule; positive, 2 joules. (198) (232)

Card Gap: 1.05 in; NG = 0.9 in. (198)

Thermal Stability:

DTA: Exo peak at 265° ; NG = 196° . (198)

Exo at 278° ; endo at 138° . (20)

Start decomp at 111° ; major exo at 274° . (75)

Weight loss and HF evolved for samples handled in
different ways; table. (76)

VTS: Less than 1 cc/gm/100 hrs at 90° . (174)

At 65° , table. (20)

Copper Block: No reaction to 250° . (75)

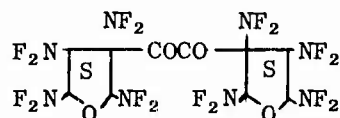
Desensitization: With 1,2-dichloroethane. (198)

Tables. (20)

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373. $C_{10}H_6F_{16}N_8O_4$



Code: OFA

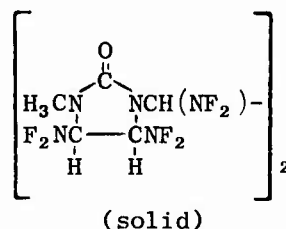
Thermal Stability:

VTS: 4.0 cc/gm/100 hrs at 90°. (94)

A pure sample exploded when ignited at 500 psi. (94)

379a. $C_{10}H_{12}F_{12}N_{10}O_2$

Code: MMBIE



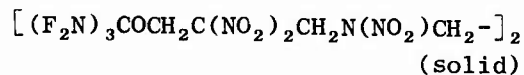
Impact: 10-20 cm; $\frac{1}{2}$ kg m.s. hammer.

Thermal Stability:

DTA: Exo at 220°. (127)

VTS: 0.2 cc/gm/100 hrs at 60°. (127)

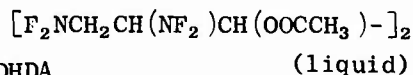
379b. $C_{10}H_{12}F_{14}N_{12}O_{14}$



Code: FA-HADD

Friction Screw: Positive at Hardness 4. (284)

380. $C_{10}H_{14}F_8N_4O_4$



Code: TDHDA

Impact: Greater than 480 kg cm; modified DuPont. (85)

Base Load Test: No. 6 lead plate. (70)

Static Sens: Deflagration at 0.26 joule. (85)

Thermal Stability:

DTA: Exo peak at 237° and 241°. (70)

Copper Block: Fumed-off in 6 min, 27 sec at 200°. (70)

Hot Bar: Fumed-off immediately at 250°. (70)

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381. $C_{10}H_{14}F_{10}N_6O_6$ $[FNHC(NF_2)_2OCHCOOC_2H_5]_2$
Code: ADET (solid)

Impact: 16 kg cm. (108)
16 kg in. (284)

Friction: Detonated with bare tools. (108)(284)

Spark Sens: Insensitive at 1.8 joules. (108)

Thermal Stability:

VTS: 0.3 cc/30 hrs at 60°; decomp product given. (108)

Autoignition: 157° (extrapolation). (108)

382a. $C_{10}H_{16}F_8N_6O_4$ $[-CH_2CH_2OOCNHCH(NF_2)CH_2NF_2]_2$
(liquid)

Thermal Stability:

Wenograd: Temp at 250 μ sec delay, 644°. (155)

382b. $C_{10}H_{16}F_{12}N_6O_2$ $(F_2N)_3CO(CH_2)_8OC(NF_2)_3$
Code: FA-OD (liquid)

Impact: 4.5 kg cm. (284)

383. $C_{10}H_{18}F_2N_2O_4$ $n-C_3H_7CH(NFCOOC_2H_5)_2$
(liquid)

Thermal Stability:

Stable on distillation and storage. (7)

384. $C_{11}H_{18}F_3N_3O_4$ $FN=C[NFCOO(CH_2)_3CH_3]_2$
Code: DC_{4n} PFG (liquid)

Impact: 4.5 cm/2 kg at 50% point: Olin. (17)

Thermal Stability:

Storable for sev. wks without decomp. (17)

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385. $C_{11}H_{18}F_8N_6O_4$

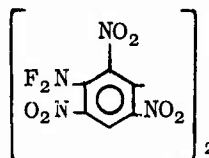


Thermal Stability:

Wenograd: Temp at 250 μ sec delay, 696°. (155)

386. $C_{12}H_2F_4N_8O_{12}$

Code: FDIPAM



Impact: 4 cm/2 kg; HMX 36 cm. (252)

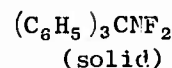
(solid)

Thermal Stability:

Stable at ambient temp for long periods of time. (204)

With usual precautions, can be easily handled. (204)

387. $C_{19}H_{15}F_2N$



Thermal Stability:

DTA: Endo at 93° and 107°; exo at 138°. (92)

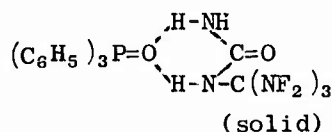
VTS: 2.3 cc/gm/100 hrs at 90°. (93)

679 cc/mole/100 hrs at 90°. (93)

0.26 cc/gm/100 hrs at 80° for 733 hrs. (200)

Stable in ethanol at 23°; unstable at 60° with slow degradation. (94)

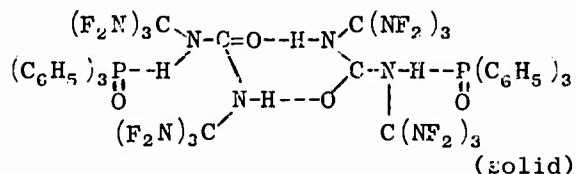
388. $C_{20}H_{18}F_6N_5O_2P$



Thermal Stability:

Dry solid dimer stable at 25° for at least 1 wk; IR unchanged for dry solid. (41)

389. $C_{42}H_{34}F_{24}N_{16}O_4P_2$



Code: BTU-TPO

Thermal Stability:

No change i. IR after 1 wk at ambient temp. (42)

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APPENDIX A

ACRONYMS - COMPOUND NUMBERS

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AAPA	140	C ₄ PFG	297
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BDMI	246	DFTDP	271
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APPENDIX B

ABBREVIATIONS

atm	atmosphere
b.p.	boiling point
Bruceton	Bruceton impact machine
BuMines	Bureau of Mines impact machine
cc	cubic centimeters
cm	centimeter
decomp	decomposition
DTA	differential thermal analysis
endo	endotherm
exo	exotherm
gm	gram
hr	hour
hrs	hours
HMX	cyclo tetramethylene tetranitramine
impact	impact test
in	inch
kcal	kilocalories
kg	kilogram
M.E.V.	man-equivalent-volt
mm	millimeter
m.p.	melting point
m.s.	mild steel
μ sec	microsecond

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neg	negative
NG	nitroglycerin
no.	number
Olin	Olin Matheson impact machine
Picatinny	Picatinny Arsenal impact machine
PbN ₆	lead azide
pos.	positive
RDX	cyclo trimethylene trinitramine
sec	second
sev	several
soln	solution
s.s.	stainless steel
temp	temperature
vs	versus
VTs	vacuum thermal stability
Wenograd	Wenograd stability test
wt	weight

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APPENDIX C

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Data from sensitivity tests made on 400 NF compounds between 1960 and mid 1966 have been compiled. The scope of the compilation includes testing information from impact, friction, static, shock, and compression test and from thermal stability measurements. Reviews on sensitivity structure relationships and on thermal decomposition mechanisms and kinetics are given in a discussion section.		

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