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15 May 1976 to 14 October 1979

DESENSITIZATION OF EXPLOSIVE MATERIALS

By: Marion E. Hill and John M. Guimont

Prepared for:

OFFICE OF NAVAL RESEARCH
800 North Quincy Street
Arlington, Virginia 22217

Attention: Dr. Richard S. Miller
Code 473

Contract No. N00014-76-C-0810 NRO93-056
SRI International Project PYU-5374

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The desensitization of explosive compounds has been studied by the synthesis and testing of analogs of selected molecular structures in which part of the hydrogen has been replaced by fluorine. The objectives were to demonstrate whether or not "chemical desensitization" could be achieved with fluorine in specific positions and groupings, to infer from the results how the fluorine affected the initiation process, and to permit the design and synthesis of high energy and relatively insensitive compounds.			

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20 ABSTRACT (Continued)

Previous work at SRI has shown that bis(2,2,2-fluorodinitroethyl) formal (FEFO) is desensitized when the aldehydic hydrogens are replaced by fluorine. To obtain information on the generality of this phenomenon, we prepared several formals and representative compounds of other classes and tested them for stability, and for sensitivity by impact and shock initiation. Thus, bis(trinitroethyl) formal and its fluorinated analog were very sensitive but data obtained in the card gap test showed decreased sensitivity by the introduction of fluorine. Tests of other formals, such as bis(difluoramino) propyl formal and its fluorinated analog showed decreased impact sensitivity for the fluorine compound but both were too sensitive for shock sensitivity tests in neat form. Two fluorinated isomers of bis(dinitropropyl) formal were studied to obtain information on the effect of the fluorine substituent position; the tests gave indefinite data as a result of test artifacts and insensitivity of some of the experimental compounds.

Desensitization of the ether, bis(fluorodinitroethoxy) ethane, was obtained by substituting the four hydrogens with fluorine; results from impact and shock initiation tests showed that the fluorine analog was definitely less sensitive and was as energetic as the hydrogen compound. A series of ethyl nitrates, in which fluorine was in the form, $-FCH_2$ and $-CF_3$, were unresponsive to initiation pressures in the wedge test; qualitative indications from these tests and impact tests seemed to show that fluoroethyl nitrate was slightly less sensitive than ethyl nitrate and trifluoroethyl nitrate was least sensitive. Other nitrates not prepared on this program had decreased sensitivity in the fluorinated form. Similarly, a nitroalkane series showed that fluorodinitroethyl fluoride was about equal to fluorodinitroethane and both were less sensitive than dinitroethane. The comparison of ethyl trinitroethyl nitramine and trifluoroethyl trinitroethyl nitramine indicated a possible sensitization by fluorine, in reverse of the expected trend.

Overall we conclude that (1) some form of desensitization can be achieved by introduction of fluorine into the ether classes of organic explosives; (2) the degree of desensitization may be very small, or may not be detectable by testing; (3) desensitization may be measurable with one type of sensitivity test but not another; (4) the degree and type of desensitization may depend on the position of the fluorine in the molecule. Insofar as testing is concerned, experience in this program showed that a suitable small-scale method that is adequate for really definitive studies does not exist.

[illegible]

The research program was performed by staff of the Chemistry

The research program was performed by staff of the Chemistry Division of the Biological Sciences Division under the supervision of

Small-scale screening tests, "wedge" tests, and "flying plate" tests

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GLOSSARY

BDNPF	Bis(2,2-dinitropropyl) formal
BFDEE	1,2-Bis(2',2',2'-fluorodinitroethoxy) ethane
DFF	Bis(2,2,2-fluorodinitroethyl) difluoroformal
DNE	1,1-Dinitroethane
EN	Ethyl nitrate
ETN	1,1,1,3-Tetranitro-3-azapentane (ethyl trinitroethyl nitramine)
FDN	1,1,1-Fluorodinitroethane
FDNEF	1,2-Difluoro-1,1,-dinitroethane
FEFO	Bis(2,2,2-fluorodinitroethyl) formal
FEN	2-Fluoroethyl nitrate
FPFO	Bis(3-fluoro-2,2-dinitropropyl) formal
HTD	1,2-Bis(2',2',2'-fluorodinitroethoxy) tetrafluoroethane
NFDF	Bis[2,2-bis(difluoroamino)propyl] difluoroformal
NFPF	Bis[2,2-bis(difluoroamino)propyl] formal
NPFF	Bis(2,2-dinitropropyl) difluoroformal
TEDFO	Bis(2,2,2-trinitroethyl) difluoroformal
TEFO	Bis(2,2,2-trinitroethyl) formal
TFEN	2,2,2-Trifluoroethyl nitrate
TFETN	1,1,1-Trifluoro-3,5,5,5-tetranitro-3-azapentane (trifluoroethyl trinitroethyl nitramine)

INTRODUCTION

The Armed Services have continuing problems with explosive materials with regard to their optimum formulation, end-use fabrication, toxicity, irregular burning, and premature detonation. Of these problems, accidental initiation of explosives because of the inherent sensitivity of the energetic ingredients has been one of the most formidable for research and technology developments to overcome. Because many approaches to the solution of hazard problems have become standardized, few new advances have been made in recent years to desensitize explosive ingredients.

In earlier work for Lawrence Livermore Laboratory, desensitization of bis(fluorodinitroethyl) formal (FEFO) was achieved by replacing the hydrogen of the aldehydic carbon, $-OCH_2O-$, with fluorine to produce bis(fluorodinitroethyl) difluoroformal (DFF).¹



DFF was as energetic as FEFO but was dramatically less sensitive, especially to initiation of low velocity detonation (LVD). In card gap tests at SRI the shock pressure required to initiate FEFO was much less (i.e., the compound was more sensitive) by several orders of magnitude than that required to initiate DFF. Table 1 summarizes the sensitivity properties of these two compounds.

In tests at Lawrence Livermore Laboratory with the wedge configuration, DFF not only showed much less sensitivity toward initiation than FEFO, but also exhibited a larger failure thickness.² (The "wedge" test consists essentially of a controlled shock pressure delivered by a donor

Table 1

SENSITIVITY PROPERTIES OF FEFO AND DFF

	<u>[FC(NO₂)₂CH₂O]₂CH₂ FEFO</u>	<u>[FC(NO₂)₂CH₂O]₂CF₂ DFF</u>
Physical state	Liquid	Liquid
Differential thermal analysis, (DTA), °C	Exotherm starts 209	Exotherm starts 228 max 250
Chemical reactivity test, (CRT), cm ^{3a}	0.04-0.1	0.04-0.06
Low velocity detonation, (LVD) ^b	1500-1800	225-325
High velocity detonation, (HVD) ^b	80-85	77
Wedge test		
LVD, threshold ^c (% PETN)	45	90
HVD, threshold ^d (% PETN)	95	100
Impact, kg-cm	6	135

^a LLL chemical reactivity test at 120°C, 22 hr.

^b Card gap test at SRI using 1/2-inch-diameter tubes.

^c "Wedge" test at LLL using 1.6 mm initial diameter; % PETN is the amount of PETN required to initiate; a low value indicates extreme sensitivity (Ref 2).

^d 3.2-mm wedge.

explosive into a thin wedge-shaped film of a liquid acceptor explosive). Thus, both high velocity detonation (HVD) and LVD were initiated in FEFO at only 45 wt% PETN equivalent energy in the booster pellet at 1.6-mm film thickness. Neither the same energy, nor indeed the energy obtained from 100 wt% PETN, would ignite DFF at the same film thickness. When the film thickness was increased to 3.2 mm, LVD in DFF was obtained at much higher input pressures, equivalent to 90 wt% PETN. Failure thickness for FEFO in the LVD mode was essentially zero at any thickness. Consequently these tests showed that pure undiluted FEFO was exceedingly dangerous (similar to nitroglycerin), but that DFF was much less hazardous by several orders of magnitude. Other physical property improvements were obtained in DFF: lowered melting point and glass transition temperature, higher density, decreased impact sensitivity, and lower toxicity.

We hypothesized that if "chemical" desensitization could be achieved by a simple replacement of H with F in one example of the formal class, then possibly other formals and other classes of explosive compounds could be similarly desensitized while retaining their energy. Such chemical desensitization is in contrast to the normal method of reducing hazard by diluting the energy with additional CH_2 groups in the molecule or by formulating energetic explosives with desensitizing matrices (another method of dilution). Heretofore, ease of initiation paralleled the energy of the explosive ingredient; that is, the most energetic compounds were the most sensitive. DFF sensitivity is an exception.

Later work on this contract under the sponsorship of the Office of Naval Research (ONR) confirmed the original observation. The emphasis of this study has been to determine whether desensitization by introducing fluorine into a molecule is a general phenomenon. The objectives of the program were to:

- (1) Prepare organic explosives having $-\text{OCH}_2\text{O}-$ and analogous $-\text{OCF}_2\text{O}-$ groups and then extend the work to other explosives by modifying $-\text{CH}_2-$ groups.
- (2) Verify that desensitization has been achieved by testing the compounds for sensitivity to initiation by shock wave and impact.

- (3) Analyze the results in terms of molecular structure to deduce how initiation is influenced by change in structure.
- (4) Explain how sensitivity is affected by changes in chemical characteristics and physical properties.
- (5) Attempt to predict how desensitization may best be achieved by the introduction of fluorine into new molecules.

This report describes the results of comparative sensitivity measurements on fluorinated and unfluorinated formals, ethers, nitrates, nitramines, and nitroalkanes. The quantitative data obtained for formals and ethers provided evidence for a general trend toward desensitization. Data for the other classes were less quantitative, but some qualitative deductions were possible. These results are reviewed in the sensitivity measurements discussion below. Evaluation of the results in theoretical terms to explain how structural changes (i.e., fluorine introduction) influence sensitivity and prediction of sensitivity changes was more difficult because the data were imprecise. Nonetheless, some mechanistic hypotheses are given for consideration.

RESULTS OF SENSITIVITY MEASUREMENTS

Background and Rationale

Because of the replacement of the hydrogens on the aldehydic carbon in FEFO produced a compound of such distinctly improved sensitivity, several other analogous pairs of formals were prepared and tested. These varied in kinds of energetic groupings such as $-\text{FC}(\text{NO}_2)_2$, $-\text{C}(\text{NO}_2)_3$, and NF_2 , and in physical state, such as the solid bis(trinitroethyl) formal (TEFO) and its fluorine analog (TEDFO). Also, a pair of fluorinated isomeric bis(dinitropropyl) formals were made for comparison with bis(dinitropropyl) formal, even though it is a detonable but relatively insensitive compound. These fluorinated compounds (FPFO and NPFF) were isomers that differed only in the position of the fluorine in the molecule, as in the $-\text{OCF}_2\text{O}$ group, which could be compared with two FCH_2- groups at the terminal positions of the alcohol moiety.

Examples of other classes of explosive compounds were prepared to determine whether fluorine substitution would produce the same trend in desensitization as in FEFO. Thus, representative ethers, nitrates, nitroalkanes, and nitramines were selected and prepared for testing. The ethers were bis(fluorodinitroethoxy) ethane (BFDEE) and its fluorine analog (HTD); the nitrates were ethyl nitrate (EN) and the corresponding fluoroethyl and trifluoroethyl nitrates (FEN, TFEN). The nitroalkane class was exemplified by 1,1-dinitroethane (DNE) and two of its fluorinated analogs, 1,1,1-fluorodinitroethane (FDN) and 1,1-dinitro-1,2-difluoroethane (FDNEF). The nitramines were exemplified by ethyl trinitroethyl nitramine (ETN) and trifluoroethyl trinitroethyl nitramine (TFETN).

These compounds are those that survived the selection process and could be prepared in quantities large enough to provide repeated measurements in testing. Many other "hydrogen compounds" and their fluorine analogs were considered for synthesis (and in some cases were

attempted) but were not pursued, principally because their preparation would evolve into a synthesis research project instead of achieving the program objectives. When both compounds were known to be either liquids or solids, selection was easier. However, some compounds were solids in the hydrogen form with melting points too far from that of the fluorine version to allow the shock initiation tests to be run in the same (i.e., liquid) physical state by melting. Similarly, solidifying a liquid test compound was not feasible in some cases. Other compounds were not tested because of other limiting physical properties such as stability, volatility, or extreme sensitivity.

The testing program was conducted in two stages. First, stability and small-scale initiation tests were conducted to provide information on how to handle the compounds and in some cases whether to proceed with synthesis. Some useful qualitative sensitivity information was obtained from these tests. The second (largest) effort in testing was applied to shock initiation measurements for low and high velocity detonation (LVD, HVD).

Three test methods were used: card gap, "wedge" test, and "flying plate" tests. The card gap was the standard shock initiation test,³ which consisted essentially of impinging a strong shock from a donor explosive into the test compound through an attenuating medium, usually brass or plastic; the SRI version used Lucite[®] as the attenuator. The "wedge" test for liquids was conducted at LLL; it was designed to impart a controlled shock pressure from a donor explosive into a thin wedge-shaped film of the test explosive. The "flying plate" test or electric gun system (also at LLL) uses electrically exploded metal foil to accelerate a plastic flying plate that provides a well-defined impact stimulus upon the test specimen. This test was used because the method was reported to be useful for solids of wide sensitivity range (PETN to TATB) and could be applied to liquids, specifically nitromethane.⁴

The most common methods used to produce less sensitive compositions are either to replace the sensitive compounds with others having fewer energetic groups per molecule or to mix (dilute) the sensitive compounds with insensitive materials. Both methods result in loss of energy.

Desensitization by the introduction of fluorine can be accomplished in some cases without loss of energy. To assure that the sensitivity reduction observed in our testing was not due to a reduction in energy, we calculated the theoretical detonation pressures and velocities for all of the test compounds (Table 2).

Initially, we used the TIGER code to estimate detonation pressures and velocities for the test compounds. In general, the TIGER code predicts that 75% of the fluorine in an explosive will be found as CF_4 in the detonation products, with the balance appearing as hydrogen fluoride. In discussions at White Oak Laboratory (WOL), Dr. Mortimer Kamlet⁵ pointed out that essentially all the fluorine should go to hydrogen fluoride during detonation. This is confirmed by experimental work conducted by D. Ornellas at LLL,⁶ who found HF among the products of explosions of nitroaliphatic and fluoronitroaliphatic compounds. Therefore, we recalculated the detonation pressures and velocities of our previously tested compounds using Kamlet's equation in which HF is the specified product.

In general, the TIGER code predicts that there will be a small loss in energy when fluorine is introduced into a molecule, whereas the Kamlet equation predicts a small increase. When TIGER code calculations were repeated for FEFO and DFF, and CF_4 was excluded as a possible constituent, DFF showed an increase in energy over FEFO, which parallels the prediction of the Kamlet equation. Other fluorine compounds gave similar results. Based on these calculations, it would seem that desensitization by the introduction of fluorine is not an artifact of energy reduction.

The measurement of sensitivity to shock initiation was the most difficult part of the project, as will be discussed in more detail below. The tests did not always provide clear-cut delineation between analogous compounds and sometimes forced a qualitative or intuitive interpretation of whether the introduction of fluorine achieved the intended purpose. The results were considered nonquantitative for various reasons: artifacts of a test made it suspect, such as in the inapplicability of

Table 2

COMPARISON OF DETONATION PROPERTIES OF COMPOUND TYPES

Compound Type	Compound	Detonation Pressure (kbar)		Detonation Velocity (m/sec)	
		TIGER	Kamlet ^a	TIGER	Kamlet ^b
Formals	FEFO	229	254	7272	7861
	DFF	213	272	6849	8009
Formals	TEFO	275	309	7831	8466
	TEDFO	207	288	6860	8233
Ethers	BFDEE	203	185	7034	6785
	HTD	183	215	6384	7114
HF-Formals	NFPF	170	196	6365	7132
	NFDF	b	211	b	7290
Nitrate Esters	EN	132	114	6679	6034
	FEN	163	163	6640	6698
	TFEN	138	192	5717	6998
Nitroalkanes	DNE	192	184	7259	7089
	FDN	182	195	6763	7183
	FDNEF	182	229	6473	7539
Nitramines	ETN	289	282	8170	8166
	TFETN	276	338	7571	8646
Formals	BDNPF	246	191	7844	6866
	NPFF	193	174	6979	6616
	FPFO	226	202	7360	6964

^aReference 7.^bTIGER code unable to calculate; probably because of high fluorine content or discontinuities in the Hugoniot due to phase changes.

plastic attenuation in card gap tests; the compounds did not have enough of the expected sensitivity to obtain clear-cut differences among analogs; the test may have been conducted too near the failure diameter of the experimental acceptor explosive; the impact test was too inconclusive; or physical form precluded comparisons. Nonetheless, we consider that, in addition to FEFO and DFF, clear-cut sensitivity delineation was obtained from tests of the ethers, and strong enough qualitative evidence for desensitization was obtained to allow conclusions to be made in the other systems. In general, therefore, the introduction of fluorine did desensitize most tested systems.

The following is a brief discussion of the results of sensitivity tests on the pairs of compounds successfully synthesized in sufficient quantities. Details of results are given in Table 3.

Formals

Comparison of FEFO $[\text{FC}(\text{NO}_2)_2\text{CH}_2\text{O}]_2\text{CH}_2$ with DFF $[\text{FC}(\text{NO}_2)_2\text{CH}_2\text{O}]\text{CF}_2$

Of the compound pairs tested during the program, this pair remain the best example of desensitization by introduction of fluorine. DFF shows reduced sensitivity to initiation of both LVD and HVD by shock and reduced impact sensitivity, as discussed above.

Comparison of TEFO $[(\text{NO}_2)_3\text{CCH}_2\text{O}]_2\text{CH}_2$ with TEDFO $[(\text{NO}_2)_3\text{CCH}_2\text{O}]_2\text{CF}_2$

The card gap tests on TEFO and TEDFO for sensitivity to shock initiation were imprecise in that LVD could be initiated in each of these compounds with the very long attenuation of 64 inches. Examination of fragments, test containers, and diagnostics indicated a difference. Both compounds were so sensitive that any desensitization toward shock could not be distinguished quantitatively, although other small-scale tests showed some reduction of sensitivity. Impact sensitivities of the solid forms especially showed that the fluorinated compound was less sensitive. However, the liquid TEDFO was quite sensitive to impact, just as liquid TNT is more sensitive than crystalline TNT. The effect of the trinitromethyl group toward initiation may be so overwhelming

Table 3

COMPARISON OF SENSITIVITY AND STABILITY PROPERTIES OF TEST COMPOUNDS

Formal	Compounds	DSC (a)	DTA (b)	Thermal Stability Vac. (c)	Impact Sensitivity J/L (d)	SH (e)	Speed Initiation Sensitivity Card Gap (No. of cards) (f)			Flying Plate Test (i)
							LYD	LYD	LYD	
PETN	[FC(MO ₂), CH ₂ O ₂ , CH ₂] Set 1	Exo. 208°		0.18-0.4		6	1500-1800	80-75	455 PETN	955 PETN
		Exo. 228°		0.10-0.24		135	225-235	77	905 PETN	1005 PETN
		Exo. 182		0.36		150 (solid)	>4400			
		None to 207°		0.25		6 (liquid)				
						>250 (solid)				
PETN	[CH ₂ C(MO ₂), CH ₂ O ₂ , CH ₂] Set 2	Exo. 181°	Exo. 215°		177					
		Exo. 181°	Exo. 210°		177					
		Exo. 202°	Exo. 200°		180					
		Exo. 187°	Exo. 223°			2-3			Too weak to test	
		Exo. 114°	Exo. 214°			6			Too weak to test	
PETN	[CH ₂ C(MO ₂), CH ₂ O ₂ , CH ₂] Set 3	Exo. 187°	Exo. 215°							
		Exo. 187°	Exo. 210°							
		Exo. 202°	Exo. 200°							
		Exo. 187°	Exo. 223°							
		Exo. 114°	Exo. 214°							
PETN	[CH ₂ C(MO ₂), CH ₂ O ₂ , CH ₂] Set 4	Exo. 187°	Exo. 215°							
		Exo. 187°	Exo. 210°							
		Exo. 202°	Exo. 200°							
		Exo. 187°	Exo. 223°							
		Exo. 114°	Exo. 214°							
PETN	[CH ₂ C(MO ₂), CH ₂ O ₂ , CH ₂] Set 5	Exo. 187°	Exo. 215°							
		Exo. 187°	Exo. 210°							
		Exo. 202°	Exo. 200°							
		Exo. 187°	Exo. 223°							
		Exo. 114°	Exo. 214°							
PETN	[CH ₂ C(MO ₂), CH ₂ O ₂ , CH ₂] Set 6	Exo. 187°	Exo. 215°							
		Exo. 187°	Exo. 210°							
		Exo. 202°	Exo. 200°							
		Exo. 187°	Exo. 223°							
		Exo. 114°	Exo. 214°							
PETN	[CH ₂ C(MO ₂), CH ₂ O ₂ , CH ₂] Set 7	Exo. 187°	Exo. 215°							
		Exo. 187°	Exo. 210°							
		Exo. 202°	Exo. 200°							
		Exo. 187°	Exo. 223°							
		Exo. 114°	Exo. 214°							
PETN	[CH ₂ C(MO ₂), CH ₂ O ₂ , CH ₂] Set 8	Exo. 187°	Exo. 215°							
		Exo. 187°	Exo. 210°							
		Exo. 202°	Exo. 200°							
		Exo. 187°	Exo. 223°							
		Exo. 114°	Exo. 214°							
PETN	[CH ₂ C(MO ₂), CH ₂ O ₂ , CH ₂] Set 9	Exo. 187°	Exo. 215°							
		Exo. 187°	Exo. 210°							
		Exo. 202°	Exo. 200°							
		Exo. 187°	Exo. 223°							
		Exo. 114°	Exo. 214°							
PETN	[CH ₂ C(MO ₂), CH ₂ O ₂ , CH ₂] Set 10	Exo. 187°	Exo. 215°							
		Exo. 187°	Exo. 210°							
		Exo. 202°	Exo. 200°							
		Exo. 187°	Exo. 223°							
		Exo. 114°	Exo. 214°							

Set 3 was not
sensitive to qualitative
measurement—
Qualitative obser-
vations indicate
poorly sensitivity
is PETN > PETN > PETN

Test too near failure
diameter; qualitative
observations indicate
PETN is less sensitive
than PETN
505 threshold voltage
was 4992; less
sensitive than PETN (5)

Table 3 Footnotes

- (a) DSC, °C at 10°C/min, in sealed pan.
- (b) DTA, run in open aluminum pan at 10°/min.
- (c) VTS, vacuum thermal stability run on 0.25 g samples at 120°C for for 22 hr. at approximately 0.1 mm.
- (d) CRT, chemical reactivity test, LLL, 0.25 g at 120°C for 22 hr in an atmosphere of He.
- (e) Impact sensitivity, LLL; standards, NG = 19.8 cm; FEFO, 50 cm; sample impacted on open plate.
- (f) Impact sensitivity, SRI; standards, HMX = 34 kg-cm and propyl nitrate, 4.5 kg-cm; impacted in sealed holder.
- (g) Card = 10 mil (0.254 mm).
- (h) Wedge Test, % PETN energy in donor required to initiate a liquid shaped in a long thin wedge, at 1/8 or 1/16 inch thickness in the receptor end.
- (i) Flying Plate Test, impact of plastic flyer exploded from a foil laminate onto a test sample; successful tests are expressed in threshold voltages required to obtain 50% fires.
- (j) In tests using 30 mil diameter bridge and 0.6 mf capacitor, PETN fired at 1750 v at 95% TMD; qualitatively one may conclude that TFETN is less sensitive than PETN.

that the introduction of fluorine had relatively little effect. In comparing this pair with FEFO, it should be noted that FEFO has F in place of nitro in the terminal positions and is less sensitive than TEFO or TEDFO. If fluorine desensitization is real, these differences would be expected. The experience gained with these compounds very definitely showed the difficulties of card gap testing and of having the test pair in different physical forms.

Comparison of NPFf [CH₃C(NF₂)₂CH₂O]₂CH₂ with NFDF [CH₃C(NF₂)₂CH₂O]₂CF₂

Impact sensitivity tests at LLL and at SRI⁸ showed that NFDF, bis[(2,2-bis(difluoroamino)propyl) difluoroformal, has significant reduced sensitivity to impact compared with the hydrogen analog, NPFf, despite the reduced thermal stability shown by DSC measurements in a confined cell.

Small-scale screening tests at LLL revealed that these compounds were too sensitive to handle in the neat form required for shock initiation wedge tests.

Comparison of BDNPF [CH₃C(NO₂)₂CH₂O]₂CH₂, NPFf [CH₃C(NO₂)₂CH₂O]₂CF₂, and FPFO [FCH₂C(NO₂)₂CH₂O] CH₂

The fact that bis(dinitropropyl) formal was reported to have a HVD regime coupled with the reported test of nitromethane with the LLL "flying plate" technique at high impact pressures provided what appeared to be an opportunity to use isomers for comparing the effect of fluorine position on sensitivity, that is, comparison of FCH₂- with -OCF₂O- by preparing the isomers NPFf and FPFO. These in turn could be compared with BDNPF, even though all are relatively insensitive. Work at LLL showed that the flying plate technique was not as well developed for liquids as originally expected inasmuch as the handling of liquids was mechanically difficult. Nonetheless, an attempt was made to use the method for this test series, modified by the use of a witness plate, with firings at maximum energy.⁹

An inert (CCl_4) and a sensitive liquid (FEFO) were fired to provide base points. The plate was bent in the CCl_4 test, and with FEFO the plate sustained a large hole. BDNPF bulged the witness plate and blew a small hole through with spalling. The fluorine analog NPFF burned unevenly and gave what appeared to be a detonation on one side and a bulge on the other. These results may have arisen from nonuniform fill, bubble initiation, or failure diameter problems. The isomer, FPFO, blew a hole through the witness plate somewhat smaller than FEFO.

Because of the difficulties in applying the technique to these compounds and of the indefinite results, LLL made the qualitative conclusion that, if the "magnitude of the reaction can be taken as an indication of shock sensitivity of the explosive, then clearly the BDNPF is the least sensitive." However, in our view since differences in initiation threshold (high threshold value, sensitive; low threshold, insensitive) were not obtainable, the results may be a measure of energy output differences reached by the time the shock arrived at the plate.

Ethers

Comparison of BFDEE $[\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OCH}_2]_2$ with $[\text{FC}(\text{NO}_2)_2\text{CH}_2\text{OCF}_2]_2$

This pair clearly shows³ desensitization to shock initiation in the HVD regime even though the difference between the 50% points is small. An LVD regime was not detected. The differences in impact sensitivity is an order of magnitude and is considered to be quite significant. The fluorine analog also was more thermally stable.

Nitrate Esters

Comparison of the Series EN ($\text{CH}_3\text{CH}_2\text{ONO}_2$) with FEN ($\text{FCH}_2\text{CH}_2\text{ONO}_2$) and TFEN ($\text{CF}_3\text{CH}_2\text{ONO}_2$)

The effect on sensitivity to impact seems to be progressive: one fluorine has a small discernible effect and three fluorines have a much larger effect. The thermal stability of TFEN is less than either EN or FEN, which is the reverse of the expected trend. All three compounds were insensitive to shock initiation in the wedge test despite our finding an earlier literature report of an LVD with EN in the card gap test.¹⁰

Nitroalkanes*

Comparison of the Series DNE ($\text{HC}(\text{NO}_2)_2\text{CH}_3$) with FDN ($\text{FC}(\text{NO}_2)_2\text{CH}_3$) and FDNEF ($\text{FC}(\text{NO}_2)_2\text{CH}_2\text{F}$)

Thermal stability was improved by introduction of the first fluorine, but was not further improved by the second fluorine. The principal effect of the fluorine at the C-1 position derives from replacement of the very acidic hydrogen without much steric change. For impact sensitivity, the first fluorine had no effect and the second fluorine had some effect. For shock sensitivity, the first fluorine had a significant effect but the second did not.

The impact desensitizing effect of fluorine appears to be additive in that the order of sensitivity for the nitrate esters is TFEN < FEN < EN. The position in the molecule at which fluorine is introduced appears to be significant and appears so far to affect impact and shock sensitivity differently. That is, a comparison of DNE and FDN shows that shock sensitivity, but not impact, is reduced in FDN. Conversely, a comparison of FDN and FDNEF shows that impact sensitivity, but not shock is reduced in FDNEF. Fluorine placed on the same carbon as the nitro groups has one effect, and fluorine placed on the other carbon has a different effect.

For all the compounds tested on this program, there appears to be a relationship between thermal stability in a confined cell and shock sensitivity; that is, those compounds with improved thermal stability have reduced shock sensitivity. However, no such relationship is apparent for impact sensitivity. In fact, for some pairs of compounds (NFPF/NFDF and EN/TFEN), the fluorinated analogs are less thermally stable and still less sensitive to impact.

Nitramines

Comparison of ETN [$\text{CH}_3\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{C}(\text{NO}_2)_3$] and TFETN [$\text{CF}_3\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{C}(\text{NO}_2)_3$]

Both ETN and TFETN are sensitive to impact, with essentially no difference in sensitivity exhibited by TFETN. Similarly, the fluorine did not seem to affect thermal stability. Either the trinitroethyl

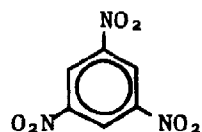
nitramine moiety is an overwhelming determinant of properties or hydrogen substitution by fluorine in a CH_3 group has no effect. At LLL the flying plate tests were run using available hardware, which dictated quantities and diameters of the test specimens.⁹ TFETN gave a distinct 50% threshold point for shock initiation.

ETN gave erratic results, which indicated to the LLL staff that the tests were run too close to the failure diameter. Thus, ETN may have fired in a diameter larger than TFETN if further testing had been possible. Furthermore, ETN provided a further problem in that its test pellets would not retain pressed density. If it is accepted that sensitive explosives have smaller failure diameters, LLL concluded that TFETN was more sensitive to shock initiation, against the expected trend and an exception to the general proposition that fluorine will desensitize.

Nitroaromatics

Comparison of Trinitrobenzene with Fluorinated Trinitrobenzenes

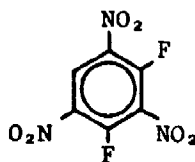
One interesting series of compounds, the trinitrobenzenes, was prepared and tested elsewhere.¹¹ MFTNB is less sensitive than TNB, but the higher fluorinated analogs DFTNB and TFTNB are more sensitive. Apparently, the fluorine substitution here does not have a simple desensitizing effect and, in fact, represents another exception to our original hypothesis of desensitization with fluorine.



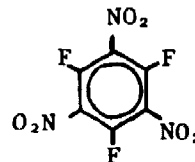
TNB
103 cm



MFTNB
138 cm



DFTNB
48 cm



TFTNB
84 cm

Test Result Conclusions and Recommendations

We consider that the test results on formals and the ether pair are sufficiently significant to confirm that the formals at least can be desensitized by introduction of fluorine at the aldehydic carbon. Substitution of fluorine elsewhere in the molecule is less conclusive for the formals and for the other classes. Thus, a $-FCH_2$ and $-CF_3$ group gave qualitative evidence of an effect, possibly desensitizing, but the tests used did not define this effect. The reversal of the trend toward insensitivity by introduction of fluorine shown by the results with the dinitropropyl series and nitramine series, of course, may lead one to conclude that the evidence overall is inadequate for generalizations. However, the test used for these two series (flying plate) had considerable difficulties with experimental artifacts, enough to frustrate the deductive process in handling the data obtained and to produce intuitive conclusions. Nonetheless, we conclude that:

- (1) Some form of desensitization, however limited, can be achieved by introduction of fluorine into an organic explosive.
- (2) The amount of desensitization may be very small or may not be detectable by testing.
- (3) Desensitization may be measurable with one type of sensitivity test but not another.
- (4) The amount and type of desensitization may depend on the position of the fluorine in the molecule, and the class of explosive.

The reader may have noted several changes in test systems used to delineate whatever differences in sensitivity fluorine may have made. Shock initiation studies were tried with three systems (card gap, wedge, and flying plate); none of these proved useful for testing both liquids and solids although the card gap had a previous history of being useful for both, and the flying plate was claimed useful for nitromethane, at least, as well as for solids. These changes in methods were dictated by the difficulty in not having available a truly definitive small-scale shock initiation test.

Scale is of course a relative term in that small scale to some is gigantic to others. The point is that chemists can seldom provide large quantities of experimental compounds. Even the wedge test, which requires the least amounts of materials, presented a problem in time and high costs to synthesize enough sample. The card gap and flying plate tests dictate the size of sample required because the tests must be conducted above the failure diameter of the explosives being tested. Other test methods (card gap, friction, and others) rank explosives on a relative basis and are not quantitative enough apparently for comparing chemical structures except in a gross sense (such as comparing TNT with HMX). That is, the organic chemist can fine-tune a molecule and provide apparent differences that cannot be discerned by current test methods. It may be that micro test methods are not possible.

Nonetheless, we recommend that research workers continue attempts to correlate methods or to refine current methods sufficiently to provide quantitative data. We feel that the "flying plate" test has the best chance for developing into a small-scale test for very sensitive experimental compounds that have extremely small failure diameters. Furthermore, comparison of different chemical structures is important enough for theoretical purposes (explanation of the initiation steps and eventually tailor-making an insensitive high energy molecule) to warrant continued investment.

THEORETICAL CONSIDERATIONS

The sensitivity of an explosive can be defined as the susceptibility of an energetic compound or composition toward initiation of an explosion by some kind of thermal or mechanical stimulus. Obviously this susceptibility has always been of practical concern to workers in the industry. The tests described above are some that are used to screen candidates and provide handling information, almost always on a relative basis and not in absolute terms. The relative sensitivity ranking of one material with another arises from the fact that an explosive may react safely toward one kind of test method stimulus and appear to be very hazardous toward another kind. Initiation stimuli are physical events, and tests have been devised to represent the following different ways of imparting initiating energy:

- (1) Thermal, characterized by heating to spontaneous decomposition, which leads to an explosion; the deflagration-to-detonation transition is an example.
- (2) Impact, in which the hazardous substance is struck a blow or given other low pressure impetus as with a hammer, bumping, or dropping.
- (3) Shock, in which an explosive is "sympathetically" detonated by a nearby explosion that imparts shock waves to the material, usually at high pressures and temperatures.
- (4) Spark, a mode most common to premature initiation of primary explosives in which a spark might be discharged from a person or other static discharge source.
- (5) Friction, in which initiation may occur from dragging or sliding an explosive against a surface; such initiation is frequently accompanied by an impact component.

All these provide sources of heat leading to a possibly correct generalization that explosions are initiated by heat, usually very localized,

a "hot spot." However, it has been suggested that initiation by shock could be explained by the mechanical breaking of a chemical bond that produces radical species that initiate an explosion. The radical production process is endothermic, and it is proposed that the exothermic reactions derive from secondary product interaction. This premise seems based on the supposition that there is not enough time for a material to react to high shock pressures and temperatures; therefore, mechanical bond breaking is a logical first step. This initiation mechanism has been challenged experimentally and by calculations, which indicate that heat buildup is indeed extremely fast.

Overall, because no one has reported a cold explosion, one may still prefer to think that initiation of an explosion is generally a thermal event; however, we are left with a basic question: What is the process whereby a molecule picks up energy (usually by a physical impetus) and translates it to an explosive reaction of great heat and pressure on the way to its thermodynamically stable products?

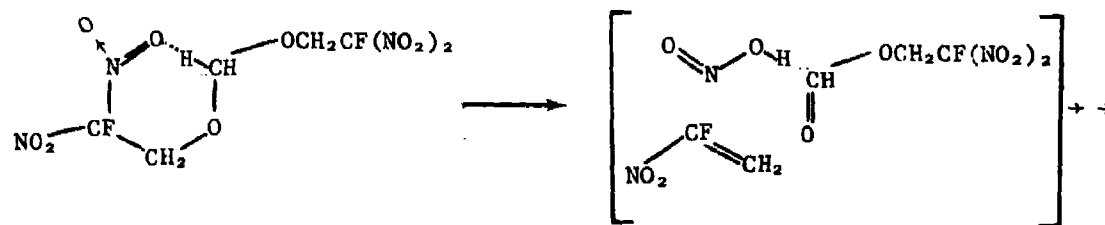
In a sense, the positive evidence that fluorine desensitizes in some cases gives credence that we are dealing with a chemical event and that chemical desensitization is achievable. Consequently, it is not unreasonable to try to explain such phenomena through basic chemical consideration just as some try to explain sensitivity and initiation characteristics by purely physical mechanisms, with minor acknowledgement of chemical factors. In regard to FEFO and DFF, which have a seemingly minor difference in structure and essentially no difference in energy, it seemed that if one could carefully and measurably decompose the molecule into preexplosive fragments there might be gross differences in these fragments. From examining these, it might be possible to make an inference about the different contribution of the fluorine to the breakdown mechanism, especially the first bond-breaking step.

We attempted to obtain information about the influence of fluorine on the bond-breaking step by using the very-low-pressure pyrolysis technique in which a controlled number of molecules are decomposed into fragments that, on an average, have no opportunity for secondary reactions.

Furthermore, through long experience obtained from studying the fundamentals of explosive systems, especially the thermodynamic and mechanistic aspects of nitroaliphatic chemistry, it is appropriate to consider a theoretical treatment of the sequence of events beginning with the bond-breaking step and subsequent immediate steps. The following two discussions address these areas.

Gas Phase Decomposition of FEFO and DFF*

The magnitude of the difference in sensitivity of DFF and FEFO leads to the natural question of why the fluorine atoms on the aldehydic carbon would have such an influence on initiation. Initiation basically begins with breaking of molecular bonds as a result of an impetus of some kind, a chemical interaction that is probably intramolecular. An examination of one molecular conformation of FEFO suggests that nitrous acid is a possible first elimination product because of the proximity of a nitro group to the aldehydic hydrogen.



Replacing the formal hydrogens with fluorine should alter the significance of this ring system and certainly would seem to influence the chemical decomposition steps leading to explosion.

We postulated that possible differences in products of the bond-breaking step may be discernible if one were able to decompose a few molecules in a controlled manner and analyze these products before any other reaction occurred. The very-low-pressure pyrolysis (VLPP) technique seemed to provide a method for achieving the controlled

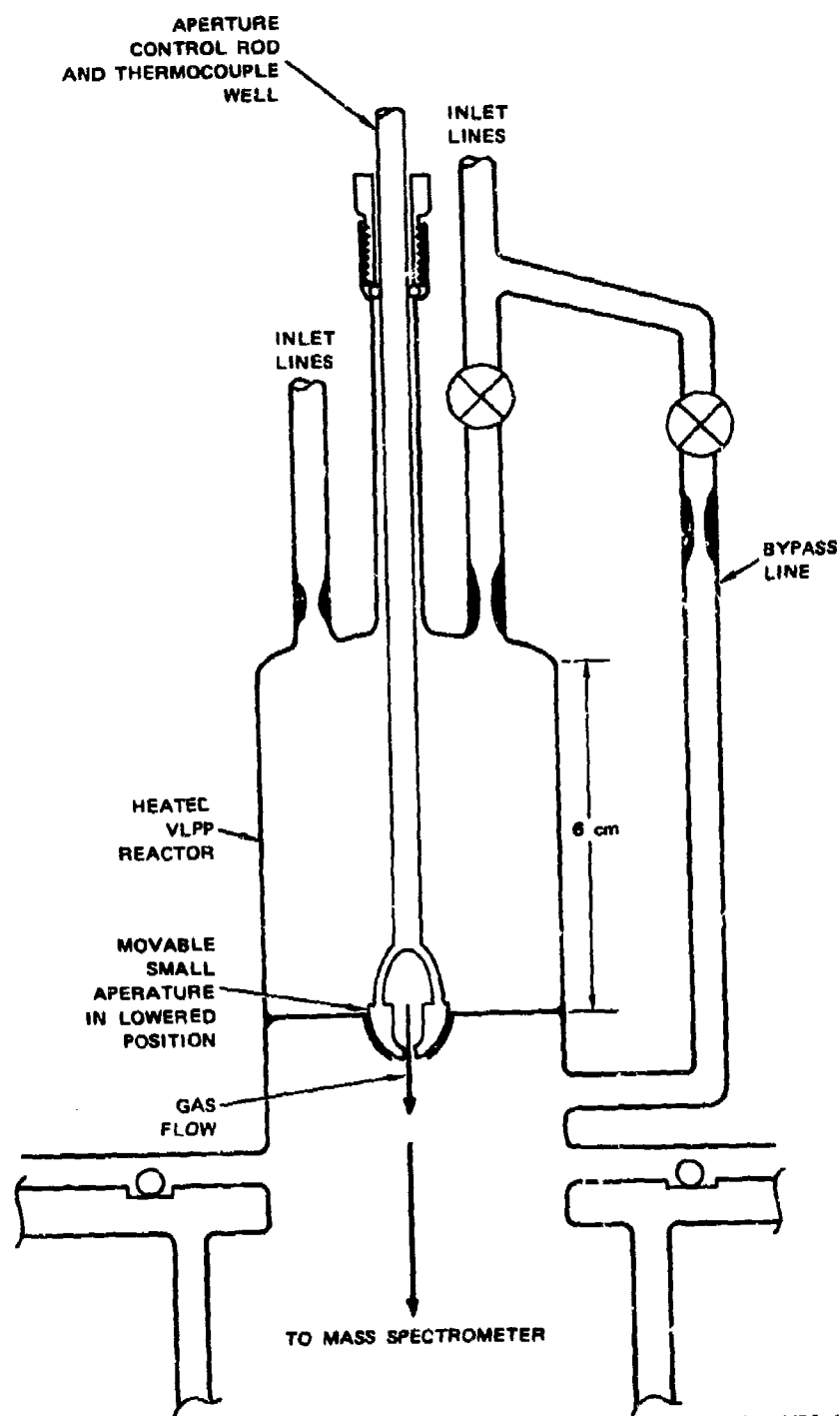
*This work was contributed by Donald McMillen

decomposition since a relatively few molecules are admitted to the reactor and, on an average, first decomposition products are analyzed without further reaction. The advantages of the VLPP technique include excellent accessibility to the initial chemical steps with minimal interference from rapid secondary reactions and a shorter residence time in the heated zone so that measurable decomposition is seen only at higher temperatures more nearly characteristic of shock temperatures than with other techniques.

Preliminary measurements of the very low pressure pyrolysis of FEFO and DFF indicate that, although the pyrolysis rates can be successfully measured, the use of electron impact positive ion mass spectrometry as the analytical tool provides limited information about the nature of the decomposition pathways. This is true for the following reasons: (1) even with the energy of the ionizing electrons lowered to ~ 35 eV, $>98\%$ of the ion intensity appears at $\leq m/e$ 65 and (2) the spectra of the two starting materials and their respective sets of pyrolysis products are very similar, being dominated in all cases by very large m/e 30 and 46 peaks. In other words, fragmentation of the positive ions produced by electron impact is so extensive that, with the currently available sensitivity, little information is provided about the nature of the pyrolysis products.

Even with this limitation, measurement of decomposition rates for FEFO and the difluorinated analog allows us to speculate about the nature of the initial decomposition step. As the data presented below will indicate, the VLPP decomposition rates of these two compounds were, in fact, found to be very similar, and yet may suggest that differences in explosive behavior are in this case traceable to differences in homolytic gas phase decomposition pathways.

Both FEFO and DFF, in spite of their low vapor pressures and probably sensitivity to surface-catalyzed decomposition, were handled quite satisfactorily with our current VLPP heated inlet system, which is shown in Figure 1. The substrate reservoir, inlet lines, and reactor were all silanized insitu at $\geq 150^\circ\text{C}$ with a hexamethyldisilazane/



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FIGURE 1 VARIABLE APERTURE VERY LOW-PRESSURE PYROLYSIS REACTOR
(Shown Without Molecular-Beam Sampling System)

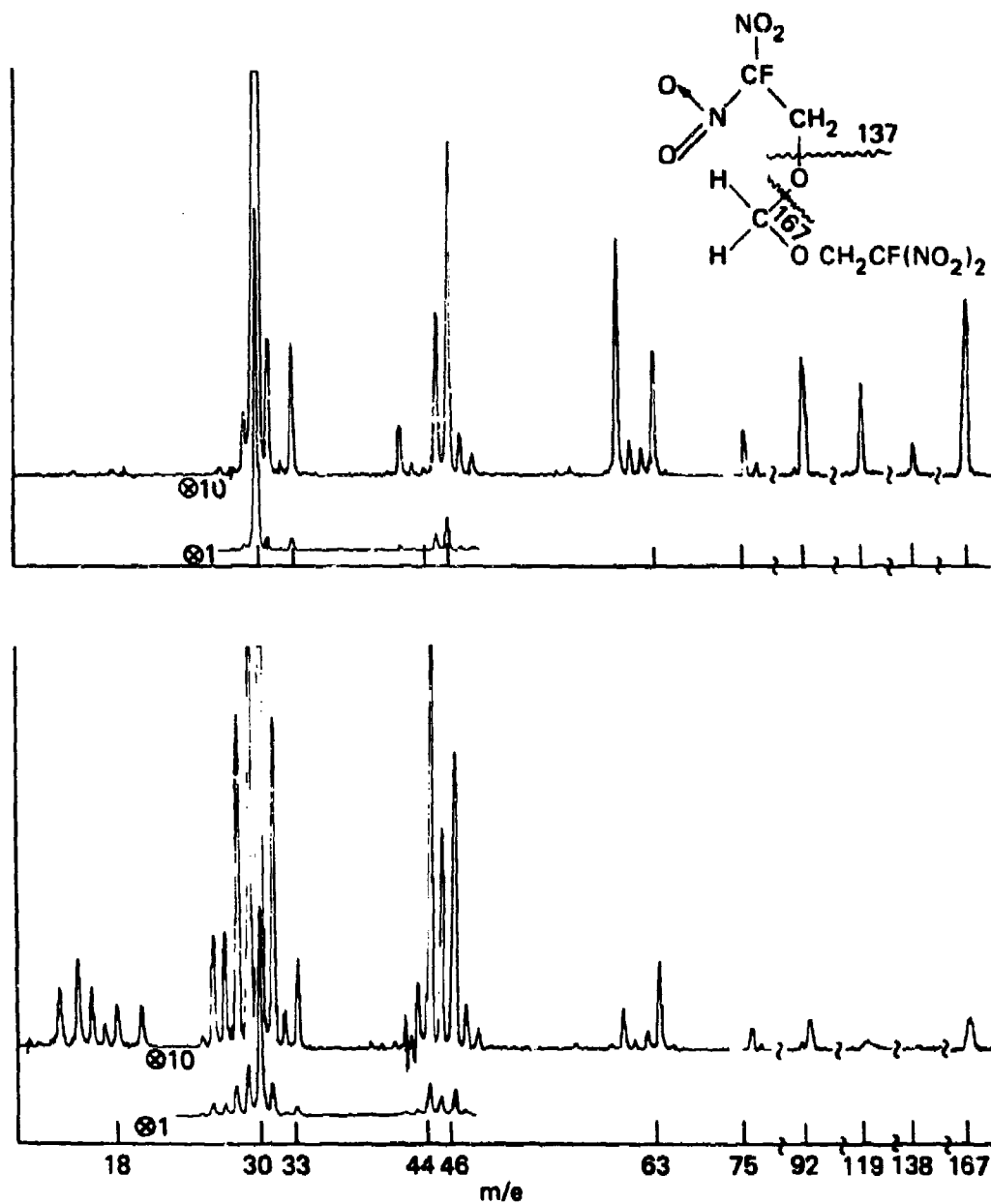
trimethylchlorosilane mixture. A satisfactory flow of even the lower vapor pressure material (FEFO) was obtained when the temperature of the substrate reservoir was kept below 145°C, where the equilibrium vapor pressure is ~ 3 torr. Spectra of FEFO and DFF and their pyrolysis product mixtures are shown in Figures 2 and 3, together with tentative assignments for the high mass peaks.

As indicated above, >98% of the ion intensity appears at m/e 65 for both FEFO and DFF. Figures 2 and 3 show that the principal difference in this low mass range is that DFF shows moderate peaks at masses 64 and 65, whereas FEFO shows negligible intensity at these masses. The high mass portions of the spectra are not exactly equivalent, but the principal features, the m/e 138 peak and the m/e 167 (m/e 167 + 36 = 203 in DFF), are similar in the two analogs.

Likewise, as Figures 2 and 3 show, the product mixture spectra are very similar, both to each other and to those of their respective starting materials. The principal feature of both is that mass 44 (presumably largely CO_2) becomes the second or third most abundant ion as decomposition increases, and masses 14, 15, 16, 17, and 26, 27, 28, and 29 become significant.

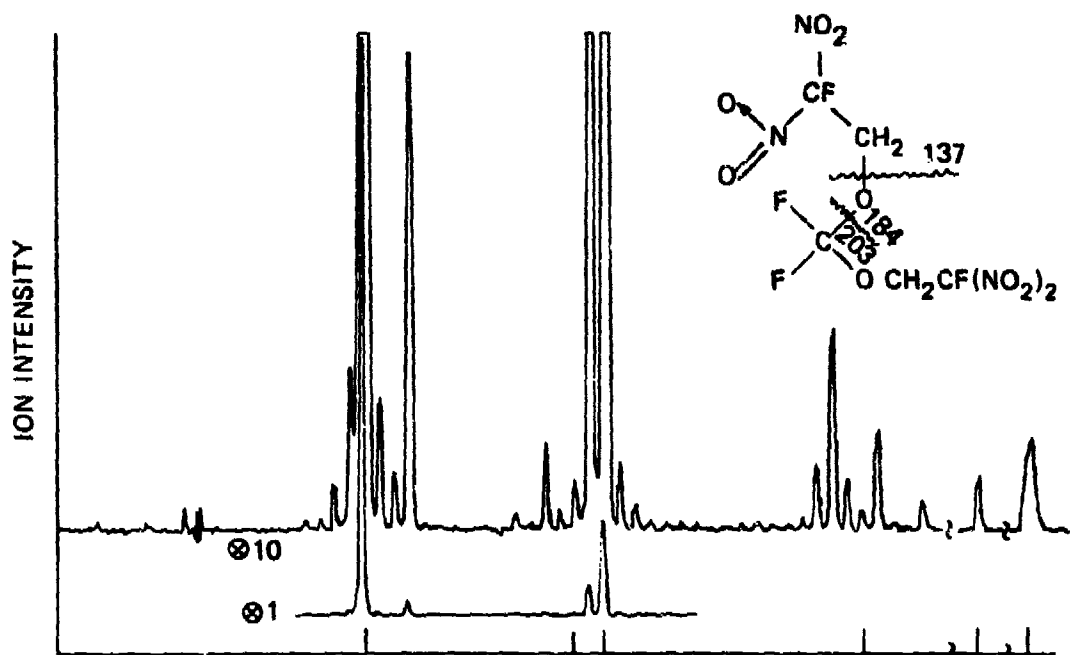
Comparisons of these spectra with those of other nitrated, fluorinated acyclic structures supports the conclusion that these highly fragmented, undifferentiated spectra are characteristic of polynitro compounds that can function as explosives. Thus, it appears likely that electron impact, positive ion mass spectrometry of this sensitivity cannot directly provide an indication of the initial steps in the gas phase decomposition of polynitro acetals.

Even with straightforward mass spectrometric identification of the initial decomposition products precluded, it was of interest merely to see whether the difference in explosive properties was parallel by a difference in their gas-phase decomposition rates. This is particularly true since the magnitude of the decomposition rate parameters can themselves provide "indirect" information about decomposition pathways. For example,

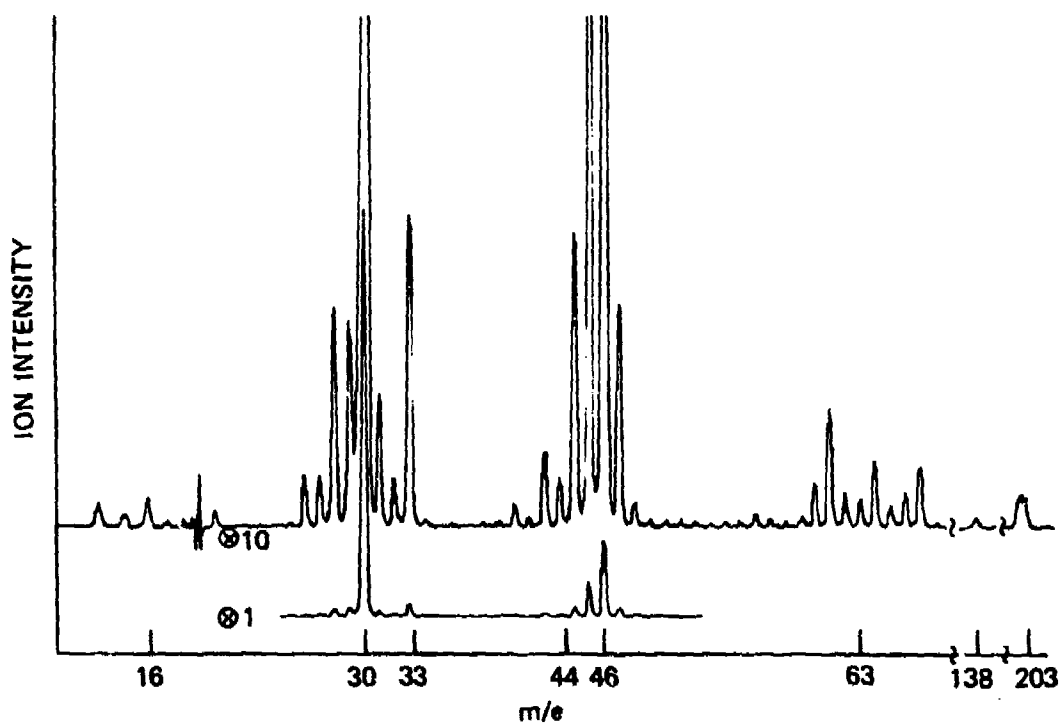


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FIGURE 2 SPECTRA OF FEFO AND ITS PYROLYSIS PRODUCTS



(a) FLOW THROUGH BYPASS



(b) FLOW THROUGH REACTOR AT 340°C

SA-5374-2

FIGURE 3 MASS SPECTRA OF DFF AND ITS PYROLYSIS PRODUCTS

a reliably determined A factor provides strong evidence as to whether decomposition proceeds by way of a simple bond fission or is a more complex process proceeding by way of a cyclic transition state. Therefore, the rates of nominal gas phase decomposition were measured over a short temperature range for FEFO and DFF.

The fractional decomposition of the starting material was determined by monitoring either mass 138 or 202. Comparison of the intensity observed when substrate flow bypasses the hot reactor and the intensity when flow is through the reactor leads directly to the rate constant for decomposition, since the flow lifetime of the substrate in the reactor is known. The decomposition rate constants for FEFO and DFF are plotted as a function of temperature in Figure 4. The data show extensive scatter, but tend to support a low activation energy process.

Although considerably more precision will be required for independent determination of both the Arrhenius A factor and activation energy, some tentative conclusions can be drawn even on the basis of the absolute rates shown in Figure 4.

The FEFO decomposition rates tend to be higher than those of DFF by a factor of about six. If all of the rate differences is ascribed to an activation energy difference, it amounts to only 2.4 kcal/mole. This is not what would be considered a large energy difference, being, for example, on the order of the 3 kcal/mole decrease which is seen for acetic acid elimination on going from ethyl- to isopropyl-acetate. In the case of FEFO and DFF one might have anticipated a greater change from a structure where a cyclic HONO elimination is plausible to one where it is completely precluded by fluorine substitution. On the other hand, there is, nothing which prevents the coincidence that in FEFO there is nearly competitive pathways (HONO elimination and C-NO₂ bond scission) and that the slightly slower one (C-NO₂ bond scission) takes over in the fluorinated analog. This, of course, would show up as a distinct slope difference in a more Arrhenius plot which is precisely determined than that in Figure 4. The question cannot, unfortunately, be answered by a "a-priori" consideration of the observed absolute rates alone. The measured values were $\sim 2 \text{ sec}^{-1}$ for FEFO 625K and $\sim 1 \text{ sec}^{-1}$ for DFF at 667K, and rate constants corresponding to plausible Arrhenius parameters for either C-NO₂ bond scission or cyclic HONO elimination fall in this same range. Thus, $\log A = 17.3$ and $E = 51 \text{ kcal/mole}$ and $\log A = 13.0$ and $E = 38 \text{ kcal/mole}$ gave, at 625K, 0.3 and 0.5 sec^{-1} for estimated C-NO₂ bond scission and HONO elimination respectively.

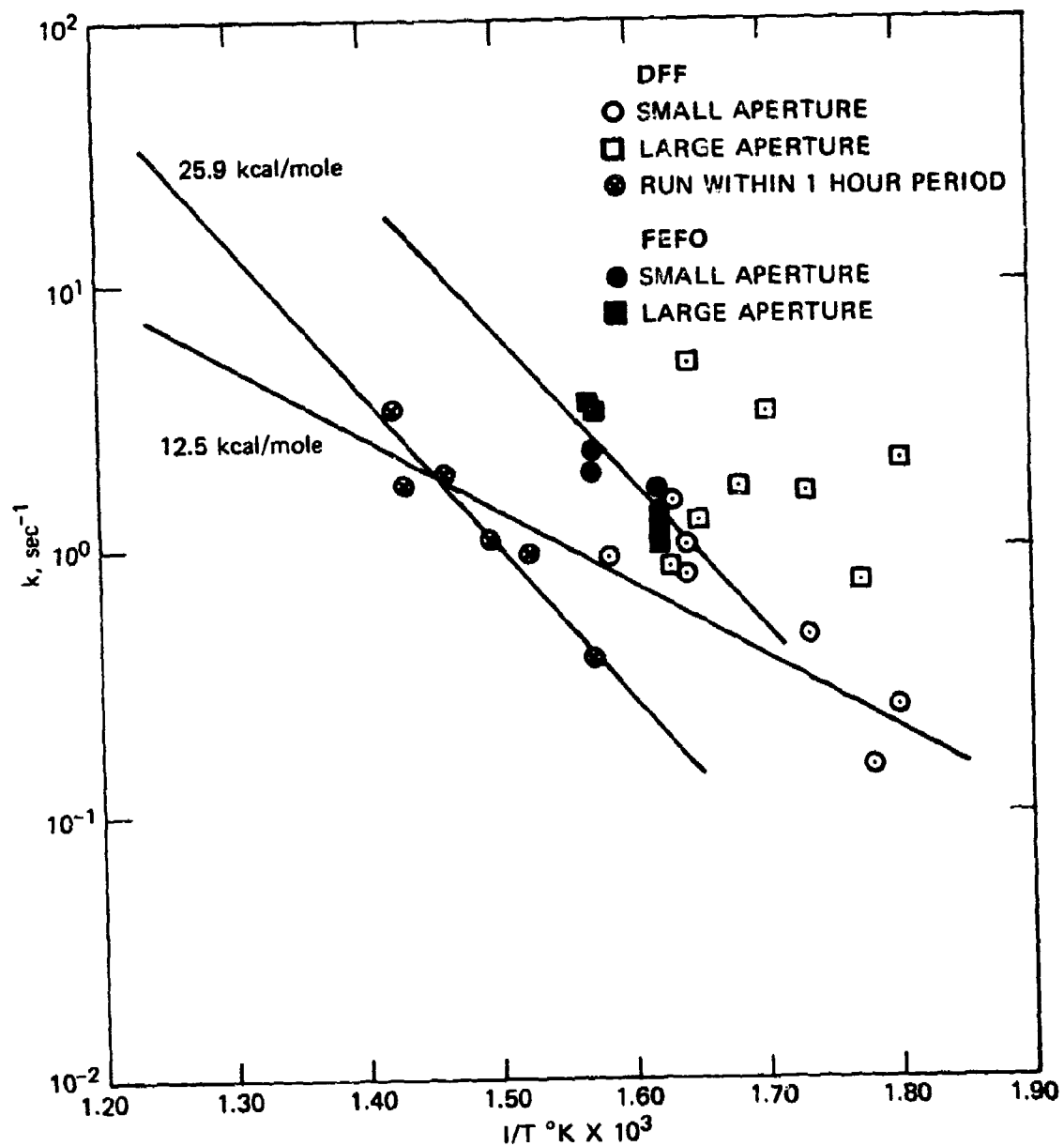
In any case, the small difference observed in gas phase rates raises the question whether the definite explosive behavior differences between FEFO and DFF are due to differences in the condensed phase decomposition mechanism which are

not observed in the gas phase. Since the initiation process in general terms is clearly autocatalytic, it is very reasonable that small rate differences in dilute phase decomposition could be substantially magnified by the more effective feedback operative during decomposition in a more concentrated phase.

The above question might be answered in part by examination of the differential thermal analysis behavior of the two materials. The difference in temperatures for the onset of the DTA exotherm of liquid FEFO and DFF is only 19°C (209 and 288°C, respectively). If the rates are assumed equal at the onset of the respective exotherms, and the different temperatures at which these equal rates occur are attributed entirely to an activation energy difference (A factors being assumed equal), then the different exotherm temperatures would result from a 4% difference in activation energies, or 2 kcal/mole for activation energies near 50 kcal/mole. Thus, the difference in initial decomposition rates in the liquid phase does, after all, seem to correspond closely to the differences in decomposition behavior observed in the gas phase; i.e., a dramatic effect of more facile feedback is not seen at this stage of liquid phase decomposition.

In summary, the results of this preliminary study of the gas phase decomposition rates of FEFO and DFF can be summarized by the following tentative conclusions:

- (1) The rates of gas phase decomposition of FEFO and DFF are observed to differ by a factor of six at 695K.
- (2) The significance of this difference is limited by the scatter of the data, but taken at face value, the measured difference corresponds to a difference in activation energy for gas phase decompositions of 2.4 kcal/mole.
- (3) This activation energy difference appears to correspond closely with the rate difference observed in the initial stage of differential thermal analysis liquid phase decomposition.
- (4) From the above conclusions it would appear that marked difference in explosive behavior observed between FEFO and DFF may well correspond to the moderate rate difference observed in the gas phase, amplified by feedback not observed either at low pressure on the gas phase or in the initial stages of the DTA liquid phase decomposition.



SA-5374-3

FIGURE 4 VERY-LOW-PRESSURE PYROLYSIS RATES FOR FEFO AND DFF

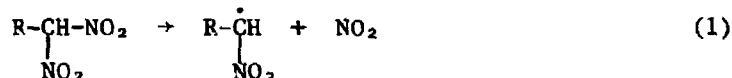
Proposed Reaction Sequence of Initiation*

Although the chemistry and physics of detonation initiation of shock sensitive nitro-materials has been studied for decades, the detailed chemical sequences leading to the ultimate violent event are not yet understood. Our interest in this topic was stimulated during a Navy-funded study of sensitivity fundamentals performed at SRI several years ago. (ONR Contract No. N00014-70-C-0190).^{1,2} Additional work was performed under ARO Contract No. DAAG29-76-C-006.

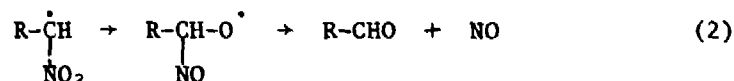
This section summarizes this brief chemical study. A reaction sequence is suggested, consistent with the observations described here, that serves to explain the source of energy leading to a steady-state detonation. We stress, however, that the material presented here has yet to be confirmed, but can serve as a model for future study.

Thermal Decomposition of a Nitroalkane

During the early sensitivity program we studied the thermal decomposition of 1,1-dinitropropane (1,1-DNP). The decomposition was studied both in the gas phase at very low pressures, and later in sealed systems at pressures up to 1 kbar. The gas phase work^{1,2}, conducted at 400°-500°C, established that the mode of decomposition was initial scission of C-N bond



followed by rearrangement and fragmentation of the organic radical



The unimolecular rate constant established for the first step was

$$\log k = 17.5 - 47/2.303 RT \text{ (sec}^{-1}\text{)}$$

*

This section was contributed by David S. Ross

In the liquid phase at autogeneous pressures in evacuated, sealed glass tubes, the compound was found to decompose at 150°-175°C at rates about three orders of magnitude faster than predicted by the unimolecular rate constant¹³. The decomposition was observed to be autocatalytic, and was promoted by the addition of water. As we shall see, the presence of water in these systems plays an important role in the proposed detonation initiation sequence.

Some of the thermal decomposition studies were conducted in a bath with a window positioned so that the heated samples could be observed visually. It was noted that when the liquid samples were placed in the bath, they rapidly became brown, and the ullage space above the liquid was similarly filled with a brown gas, most likely NO₂. It would appear then that the initial chemical process is the thermal production of NO₂, which is present both dissolved in the liquid and in the ullage space. Curiously, if the samples were removed at this point, the brown color disappeared as the tubes cooled and a colorless liquid simultaneously condensed on the walls. The process was reversible, NO₂ being immediately regenerated when the tubes were replaced in the bath. The reaction products isolated included those resulting from a complex redox system involving NO_x, namely, H₂O, CO₂, CO, N₂, N₂O, propionic acid, and acetic acid.

In similar experiments above 220°C, the samples violently exploded after a quiet period. In a series of runs at temperatures increasing up to 270°C, the times to explosion were found to decrease as the temperatures were increased. The time-temperature profile followed an Arrhenius behavior, presenting a linear relationship when considered in terms of log time vs 1/T. This finding suggests the quiet period before explosion involves some sort of kinetic process significant to the ultimate explosive event.

High pressure experiments were performed where samples of 1,1-DNP were heated at a pressure of 1 kbar. In this case the same two regimes were observed, that is nonviolent decomposition of lower temperatures, and explosive decomposition at higher temperatures. But the processes were shifted by the application of pressure to lower temperatures. At a given temperature, the rate of

thermal decomposition was significantly increased over that seen at autogeneous pressures. The explosive behavior at 1 kbar now began at about 155°C, in contrast to > 220°C for the lower pressure case. This work was performed in FEP tubes, and in some runs we fortuitously stopped the process apparently just before the explosion. In these cases, the plastic tubes were glazed and coated with a carbonaceous char, evidence of a runaway thermal reaction.

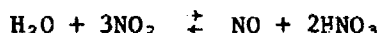
The overall picture then is of an autocatalytic redox system involving NO_x species as oxidant(s). The reaction is promoted by the addition of water and the application of pressure. The chemistry apparently leads to a highly exothermic process, and under confined conditions, the reaction system ultimately leads to an explosive event. Nitrogen dioxide is an initial product, disappearing reversibly at lower temperatures. The nitrogen products isolated from the thermal decomposition are N₂ and N₂O, with NO notably absent.

Nitric Acid as a Reactive Intermediate

The rapid and reversible disappearance of NO₂ as described above is a curious observation and suggests that a disproportionation of NO₂ is taking place. The well known hydrolysis of NO₂ to nitrous and nitric acids



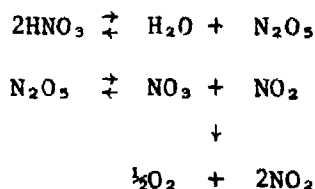
could explain the observation, since the equilibrium constant for the gas phase case increases with decreasing temperature, that is, $\log K_p(227^\circ\text{C}) = -4.2$ to $\log K_p(27^\circ\text{C}) = -1.9$.¹⁴ However, nitrous acid itself is unstable, and the net process, to be discussed below, is



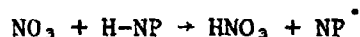
This equilibrium is also shifted to the right with decreasing temperature. These modes of NO₂ conversion do not explain the system completely, however, since for both cases the left sides of the equilibria are still favored at room temperature. Only very large quantities of water could bring about the entire disappearance of NO₂.

Nonetheless at least a qualitative picture of the system includes significant formation of nitric acid, with the subsequent formation of some very reactive intermediate. Accordingly, experiments were performed in which freshly prepared samples of 100% nitric acid were heated at 100°C in sealed, evacuated tubes with a hydrocarbon. Runs with NO₂/N₂O₄ were performed as well. The hydrocarbon used was neopentane, (CH₃)₄C, chosen because it is typically unreactive with active free radicals such as peroxy (ROO•), methyl (CH₃•), and t-butoxy ((CH₃)₃CO•).¹⁵ All of its C-H bonds are strong, with D(C-H) = 98 kcal/mole.¹⁶ The results are summarized in Table 4.

It is apparent from the data that neopentane does not react readily with the NO₂/N₂O₄ system at 100°C. That observation can be anticipated since the abstraction of H from neopentane by NO₂ is endothermic by about 20 kcal/mole. However, reaction with HNO₃ proceeds readily and is consistent with the generation of a very reactive intermediate from the thermolysis of the acid. A proposed route for the thermal decomposition of nitric acid is¹⁷



It is clear that NO₃ could play a role in the reaction with neopentane (H-NP). Thus



is exothermic by 0-2 kcal/mole and becomes a likely reaction route. The production of oxygen is anticipated from the above decomposition scheme, and it is seen that the rate of nitric acid decomposition is roughly four times the rate of neopentane oxidation.

The details of the entire picture are of course not yet clear; however, the observation of neopentane oxidation in the HNO₃ suggests that nitric acid could be an important intermediate in shock initiation of nitro explosives.

Table 4

REACTION of NEOPENTANE
with NITRIC ACID and $\text{NO}_2/\text{N}_2\text{O}_4$ ^a

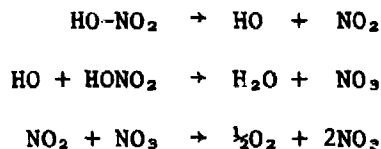
Reaction System	% Neopentane Decomposition ^b	O_2 (μmoles)
Nitric acid	24	115
$\text{NO}_2/\text{N}_2\text{O}_4$	< 1	tr
Nitric acid ^c	--	100

^aThe reactions were conducted at 100°C for 1 hour in evacuated glass tubes, with about 5000 moles of freshly prepared 100% nitric acid or about 3600 μmoles of N_2O purified N_2O_4 ; 125 μmoles of neopentane were used.

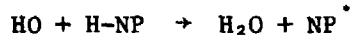
^bFractional loss of neopentane. The gaseous reaction products were CO_x and NO_x . No other products were identified.^x

^cNo neopentane used.

An additional supportive factor here is the strong possibility that a second mechanism for nitric acid decomposition may be operative.¹⁷ This scheme involves the initial generation of OH.



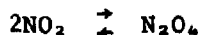
The net reaction is the same as that for the scheme discussed above. However, the possible presence of the very reactive OH provides an even more energetic route for H abstraction, since



is exothermic by 16-18 kcal/mole.

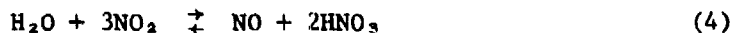
Effect of Pressure

The pyrolysis work with 1,1-DNP showed that the application of pressure has a substantial effect on the rate of nitroalkane decomposition and on the occurrence of an explosion. Accordingly, it is appropriate to consider the effects of pressure on some critical step in the decomposition process. Since NO₂ is an initial pyrolytic product, a clear choice for a substantial pressure effect is the equilibrium



where an increase in pressure favors formation of the tetroxide.

A simple exercise shows the potential importance of the position of this equilibrium. If we accept the possible critical role of nitric acid in the overall process, we can show that for equilibrium (4)



$$\log K_p(27^\circ\text{C}) = -2.6$$

$$\log K_p(227^\circ\text{C}) = -4.8$$

where NO₂ is the major component of the nitrogen dioxide-tetroxide systems, an increase in temperature decreases the equilibrium quantity of nitric acid.¹⁴ If we then shift attention to a system of the same stoichiometry,

where $N_2O_4 \gg NO_2$,



$$\log K_p(27^\circ C) = -3.7$$

$$\log K_p(227^\circ C) = -0.2$$

then, conversely, an increase in temperature increases the nitric acid formation.

Further increases in temperature drive equilibrium (4) farther to the left and equilibrium (5) farther to the right, and it thus becomes clear that a detailed analysis of the NO_x/H_2O system over a large series of temperatures and pressures could provide some significant insight into the chemistry of shock initiation. Accordingly, we applied the computer program designed by Gordon and McBride¹⁸ for calculation of complex equilibria under extreme conditions.

The calculation was performed for the $H_2O/NO_2/NO/HNO_3$ stoichiometry in equilibria (4) and (5). The results of the calculation, shown in Figure 5, confirm our expectation. With increasing pressure, the relative quantities of nitric acid increase to a significant fraction of the total nitrogen. The peak in nitric acid quantity is between 300° and $500^\circ C$, and even at pressures as low as 1 kbar, about 10% of the nitrogen is converted to nitric acid.

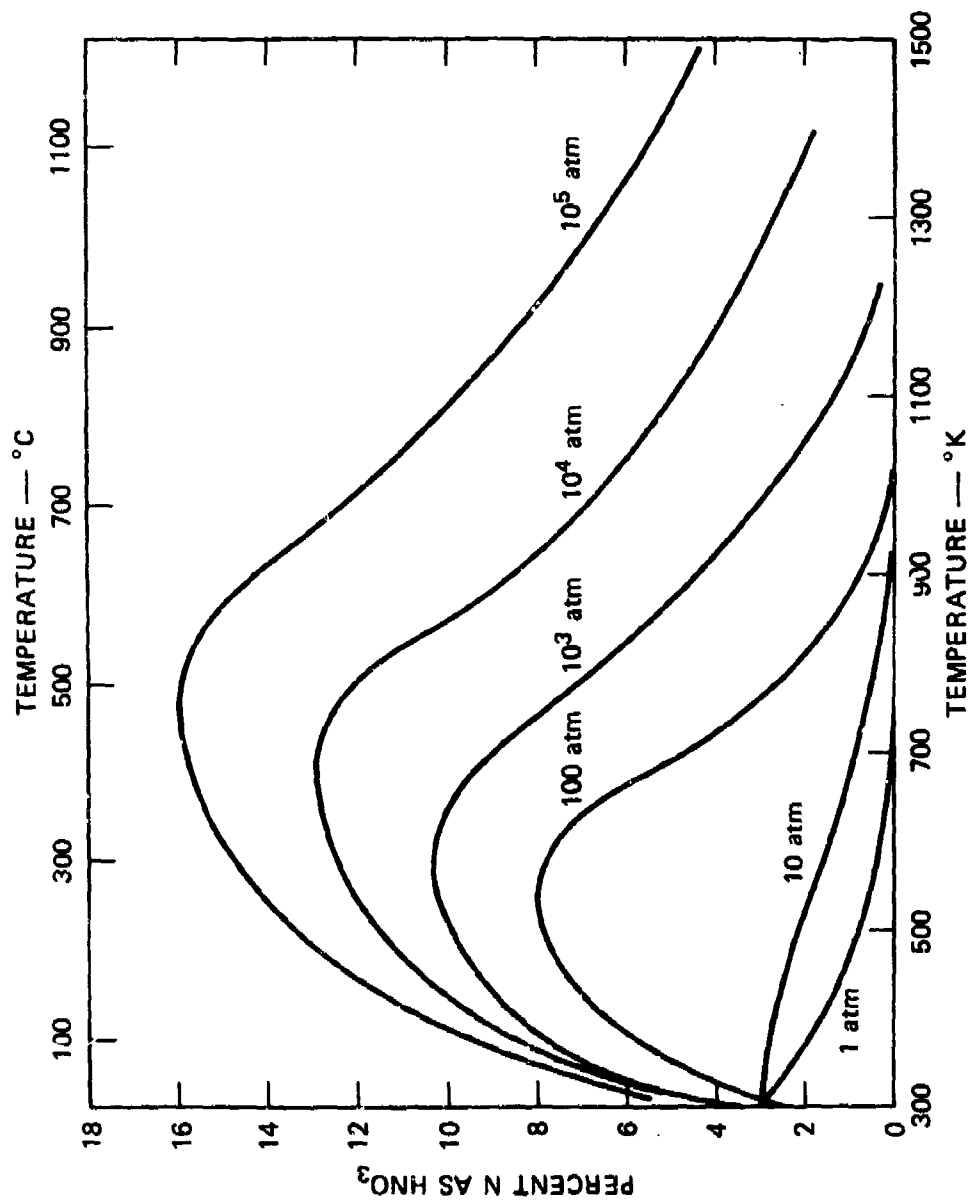
Model for Detonation Initiation

We can now propose a chemical sequence involving the chemistry of nitric acid, with the goal being an exothermic chain process. The first or initiating step in the sequence is the homolysis of the relatively weak HO-N bond in the acid, yielding reactive OH



Then for RH as the nitroalkane we can propose a chain process





SA-5374-4R

FIGURE 5 RELATIONSHIP OF PRESSURE TO NITRIC ACID FORMATION

We are not aware of reports of a reaction like (8). In fact, the gas phase free radical reactions of HNO_3 are unstudied and represent an interesting area for research. However, the step is about 9 kcal/mole exothermic and is therefore a reasonable one to propose. The entire chain process (7)-(8) is about 24 kcal/mole exothermic and thus serves as a significant source of chemical energy.

An additional favorable feature of the model is that RONO should readily decompose under the prevailing conditions



and with RO being generally more reactive toward hydrogen abstraction than R , the process at this point becomes chain branching and even more energetic.

In conclusion, it appears that a model for the chemistry taking place during shock initiation of nitro explosives includes:

- The initial thermal formation of NO_2 and H_2O .
- The conversion of NO_2 at high pressures to N_2O_4 and its hydrolysis to HNO_3 .

The thermal decomposition of HNO_3 yielding OH , which initiates an exothermic, branching chain process.

Although this proposition remains untested, the evidence supporting the scheme seems sound. It is hoped that the opportunity for a direct test of the proposed chemical sequence will become available.

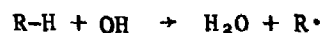
Application of the Model

The proposed model can now be used to consider the effects of replacing hydrogen with fluorine. There are two steps in which the substitution could play a role: the initial thermal C-N scission and the subsequent abstraction of hydrogen by either OH or NO_3 .

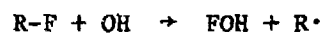
The literature indicates that -F substitution makes little difference on the rate of C-N scission. Thus for the pyrolysis of $\text{CH}_3\text{CH}(\text{NO}_2)_2$ and $\text{CH}_3\text{CF}(\text{NO}_2)_2$, the first-order rate constants are virtually

identical, being respectively $\log k(\text{sec}^{-1}) = 16.7 - 47 \times 10^3/2.303RT$ and $\log k(\text{sec}^{-1}) = 17.0 - 48 \times 10^3/2.303RT$.¹⁹ We would therefore expect that similar substitution would do little to affect the shock sensitivity of nitro compounds.

For the abstraction of hydrogen by OH or NO₂, however, there should be a substantial effect because the fuel in the molecule, the hydrogen, is being replaced by an inactive substituent. Thus we have recognized above that for R-H, the reaction



is substantially exothermic and contributes significantly to the net energetics of the model. For R-F, however, the reaction



is about 50 kcal/mole endothermic, and the F-atom transfer is clearly ruled out as significant. Successive substitution of fluorine for hydrogen, then, in terms of our model, should provide a decreased shock sensitivity.

METHODS OF PHYSICAL PROPERTY AND SENSITIVITY MEASUREMENT

Vapor Pressure

Vapor pressures of compounds with low volatility were measured by the Knudsen⁹ method, and for most of the compounds, the reported value at 25°C was determined by extrapolation from values measured at higher temperatures. For the more volatile compounds, vapor pressure was determined by measuring the boiling points at various pressures and extrapolating to 1 atmosphere.

Density

Liquid densities were measured directly using a Fisher-Davidson gravitometer. Solid densities were measured by suspending the material in a mixture of liquid nonsolvents and varying the ratio until the solid was dispersed evenly and the liquid and solid densities were the same. The liquid density was then measured with the gravitometer.

Thermal Stability

The thermal stability of the test compounds was determined by two methods. First, differential thermal analyses (DTA) were run using an open pan in air: however, some of the compounds were low boiling and exhibited only endotherms at the boiling point. Second, differential scanning calorimetry (DSC) was run at LLL on each compound under a nitrogen atmosphere in a sealed holder. Because the sample holders were sealed, the materials could be heated beyond their boiling points to observe their decomposition temperatures.

Impact Sensitivity

Impact sensitivity measurements were made using two types of machines having different physical arrangements. Tests at SRI were made on a Technoproducts Dropweight Tester. Solid samples are held in a brass cup placed under a smooth steel piston. Liquid samples are confined in a steel chamber sealed with an O-ring and rupture disc. Tests at LLL were run using a machine in which the sample is placed on an open plate. No real parallel can be drawn between the two test methods or between test results on liquids and solids run on the same machine.

Shock Sensitivity

Three methods were used to determine the shock sensitivity of test compounds: the card gap test³, the "wedge" test², and the "flying plate" test⁴.

Card Gap Test³ In this test a donor explosive (tetryl) is used to generate a strong shock (~200 kbar). The strength of this shock wave is reduced by placing a gap of plastic (plexiglas disks or cellulose acetate cards 0.01 inch thick) between the donor explosive and the material to be tested until a detonation no longer occurs. The larger this gap, the lower the input pressure to the sample. Results are reported as the minimum number of cards or inches of gap necessary to prevent detonation in the materials (100 cards = 1 inch). The test compounds are confined in steel tubes 1/2 inch in diameter and 4 inches long.

Results of the test were determined by two methods. In the first, a witness plate was placed over the open end of the sample tube. A fragmented witness plate and sample holder indicated a high velocity detonation (HVD), a witness plate with a hole punched and an intact sample tube indicated a low velocity detonation (LVD), and an undamaged witness plate indicated no detonation. In the second method, a witness plate was used, and pressure gauges were placed at the top and bottom of the sample

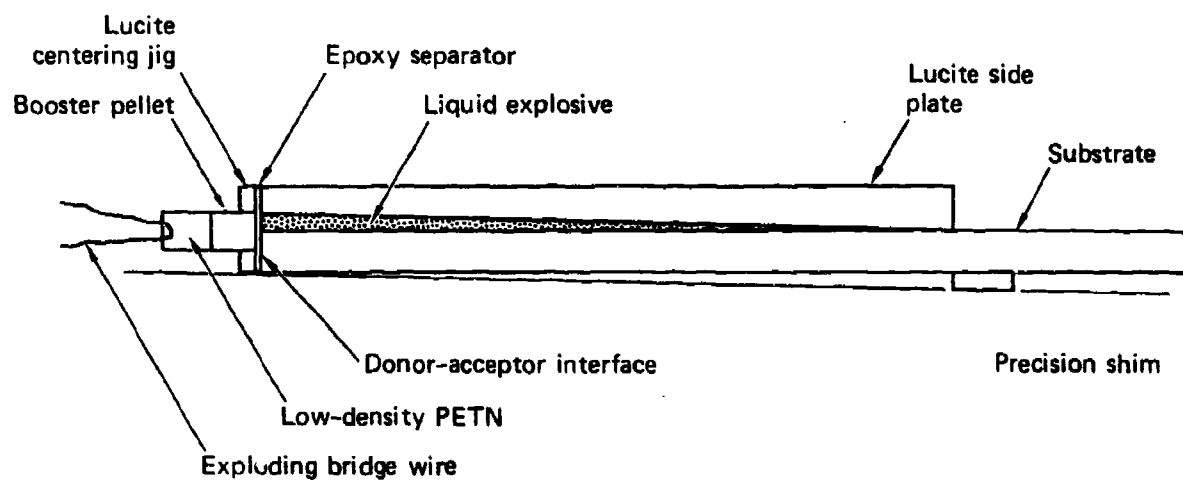
tube. Measurement of the output pressure and the time lag between the input and output shock waves defined the results of the test.

"Wedge" Test² This test arrangement consists of a flat shot tray of 6061-T6 aluminum alloy plate 12.7 mm thick, 50.8 mm wide, and 380 mm long. Polymethylmethacrylate (PMMA) was used on the sides, and a 0.5-mm-thick piece of epoxy was fixed to one end to confine the liquid on the plate. A PMMA fixture was used to align the detonator-booster assembly on the closed end of the plate with its center on the liquid-aluminum interface (Figure 6).

The shot tray was leveled on the table and then shimmed so that the open end was elevated either 1.6 or 3.2 mm. Liquid was added to form a long, thin wedge tapering from either 1.6 or 3.2 mm thickness at the initiator end to zero at a position 305 mm along the plate. The aluminum base became a witness plate that clearly showed the various reactions occurring during the test.

The donor system consisted of an exploding bridgewire detonator filled with low-density PETN ($\rho = 0.95 \text{ g/cm}^3$), a booster pellet 12.7 mm in diameter by 12.7 mm long, and a 0.5-mm epoxy attenuator. The booster pellets consisted of blends of PETN and pentaerythritol pressed to $90.0 \pm 0.5\%$ of their theoretical maximum density. The PETN concentration ranged from 20 to 100 wt% in 5% increments, giving a variable output donor. Lower concentrations of PETN could not be made to detonate reliably. The input pressures of the donors were previously determined and ranged from 50.7 to 185 kbar.

The results of each shot are based on the condition of the aluminum plate after the shot. High velocity detonations (HVD) leave a definite depression in the plate, low velocity detonations (LVD) cause scratching and pitting of the plate, burning of the sample leaves the plate dry, and a "no go" leaves a wet plate. Samples that will not detonate using a 1.6-mm wedge (presumably because of a greater failure thickness) are subjected to testing with the 3.2-mm wedge.



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FIGURE 6 SHOT CONFIGURATION FOR LLL LOW-VELOCITY DETONATION TEST

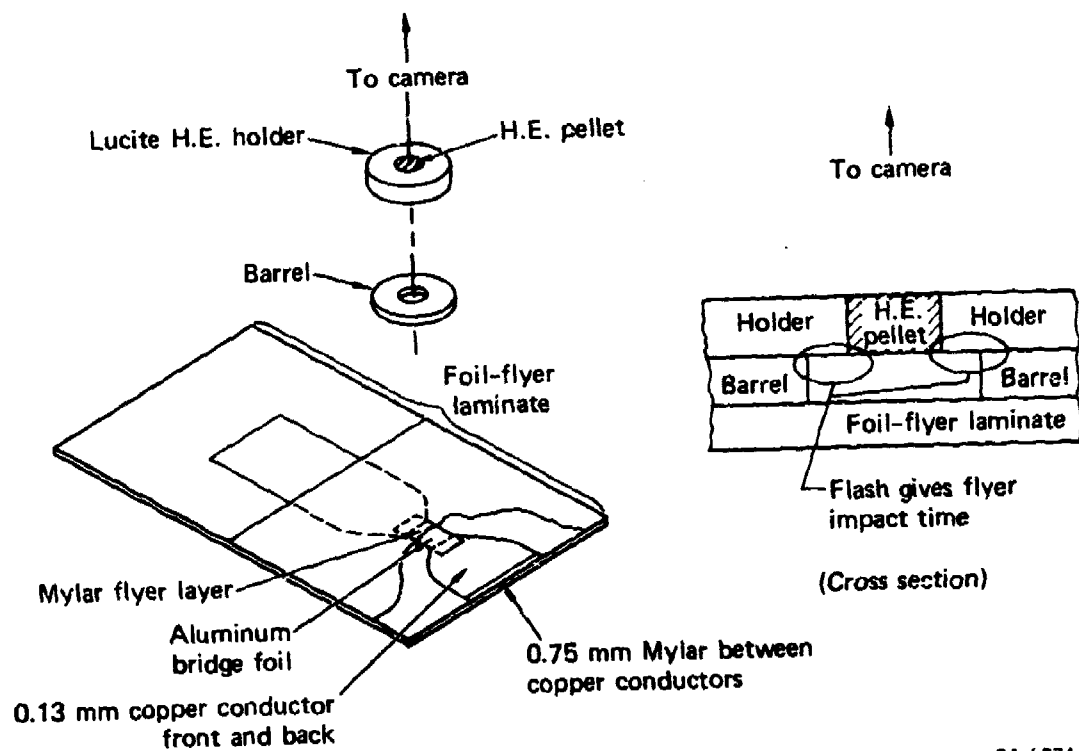
"Flying Plate" Test⁴ This system was used for studying initiation properties of explosives at LLL,⁴ and attempts were made to adapt it as a sensitivity test for the nitramine solids and the dinitropropyl formal liquids. For solids, the method uses an electrically exploded metal foil that drives a plastic "flyer" laminated to it down a barrel (Figure 7). The "flyer" impacts the experimental explosive with a well defined pressure stimulus that initiates the sample. Optical and electrical diagnostics are used to measure the energy transmitted and time of initiation of the sample. Impact pressures and pulse widths can be varied over a broad range, and explosives of varying shock sensitivities can be studied. Results of initiation experiments have been reported⁴ for PETN, TATB, PBX-9404, and nitromethane, which vary widely in sensitivity toward shock initiation.

Detonation Pressure and Velocity

Theoretical detonation pressures and velocities were calculated using the TIGER code. TIGER is a digital computer program in FORTRAN IV for calculating detonation parameters of condensed explosives. The central problem is the calculation of conditions in the Chapman-Jouget (C-J) detonation wave. Subsidiary problems are calculations of the properties of the detonation products along the Hugoniot curve, along isentropes (or along curves where other variables are held constant) or at specified points or grids of points. TIGER may also be used for detonations in gases and for direct solution of chemical equilibria at specified values of two state variables.

The program includes 36 subroutines whose interconnections are such that effective separation is maintained between the hydrodynamics, the thermodynamics, and the equation of state.

As currently arranged, the program can consider up to 30 gaseous constituents and up to 10 solid constituents of the product mixture. Up to 10 chemical elements may enter into the makeup of these product substances. In addition to solving chemical equilibria for the mole numbers of the constituents, the thermodynamic part of the code calculates



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FIGURE 7 DIAGRAM OF SYSTEM USED FOR "FLYER" INITIATION STUDIES

the complete thermodynamic properties of the mixture and the first partial derivatives. Along an isentrope, the Riemann integral and the enthalpy increment are calculated for each step of expansion.

Initially, TIGER was unable to determine the C-J point because 29 gaseous constituents were being considered. We found that the computations could be done only after some of the gases were rejected as possible constituents and the most abundant gaseous products were stipulated. Rejected gaseous products were C_3H_8 , C_2H_6 , C_2H_2 , C_3H_6 , CH_2 , CH , F_2 , F , F_2O , and NF_3 . The gaseous products considered by TIGER were CO_2 , N_2 , H_2O , HF , CF_4 , CO , O_2 , NO , CH , H_2 , O , NH_3 , H , CF_3 , N , CF_2 , CH_4 , CH_3 , and C , with the first six being specified as most abundant.

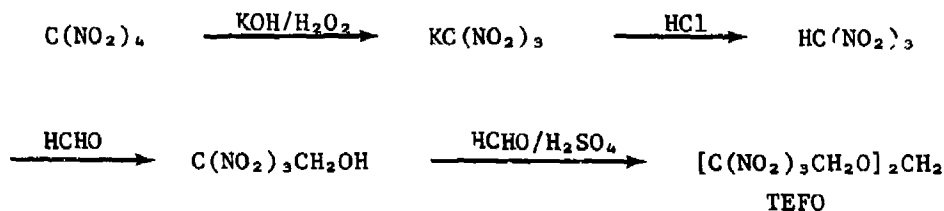
In general, the TIGER code predicts that 75% of the fluorine in an explosive will be found as CF_4 in the detonation products, with the balance appearing as hydrogen fluoride. During discussions with Dr. Mortimer Kamlet⁵ at WOL, it was pointed out that essentially all the fluorine should go to hydrogen fluoride during detonation. This is confirmed by experimental work conducted at ILL⁶. Therefore, we recalculated the detonation pressures and velocities of the test compounds using Kamlet's equation in which HF is the specified product. The results are given in Table 2.

SYNTHESES OF EXPLOSIVES FOR SENSITIVITY TESTS

All the compounds tested during this program were prepared in our laboratories. General descriptions of their syntheses are given below. Detailed experimental procedures for the preparation of previously unknown compounds were given in earlier reports, as referenced in each Section. Physical properties are summarized in Table 5.

Bis(Trinitroethyl) Formal (TEFO)

TEFO was prepared using the reported²⁰ procedure, as shown in the following equations:



During this program, 429 g (249 ml) of TEFO was prepared, most of which was consumed in card gap tests.

Bis(Trinitroethyl) Difluoroformal (TEDFO)

TEDFO was prepared according to the following equations:

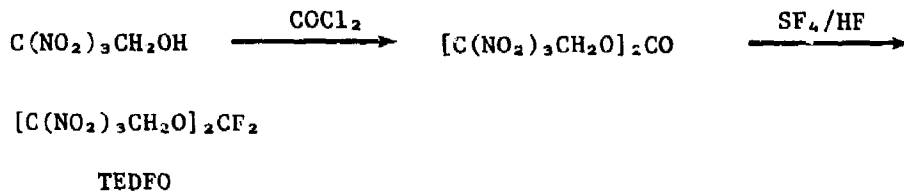


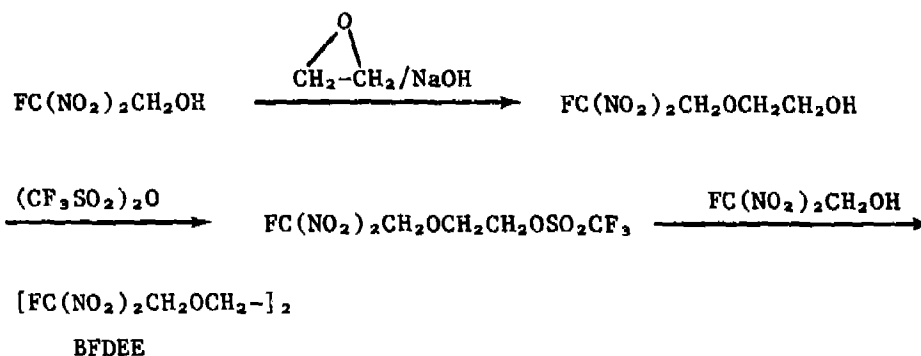
TABLE 5
PHYSICAL PROPERTIES OF TEST COMPOUNDS

COMPOUNDS	Mol Wt.	b.p., °C (mm)	m.p., °C	Density g/cm ³	v.p., mm	Δ H _f , kcal/mol	Sound Speed, m/μsec	Compressibility cm ² /dyne (x 10 ⁻¹¹)
<u>Formals</u>								
FEFO [FC(NO ₂) ₂ CH ₂ O] ₂ CH ₂	320.0	110(0.3)	14	1.59	1.6 x 10 ⁻⁴	- 178	1.25	4.03
DFF [FC(NO ₂) ₂ CH ₂ O] ₂ CF ₃	356.1	70(0.003)	- 17	1.67	1.6 x 10 ⁻³	- 275	1.15	4.53
TEFO [(NO ₂) ₂ CCH ₂ O] ₂ CH ₂	374.2		65	1.72	9 x 10 ⁻⁴	- 151	1.31	3.39
TEDFO [(NO ₂) ₂ CCH ₂ O] ₂ CF ₃	410.2		16-18	1.68	7.5 x 10 ⁻³	- 243	1.17	4.35
BNMFF [CH ₂ C(NO ₂) ₂ CH ₂ O] ₂ CH ₂	312.2		33	1.56		- 143		
NPMFF [CH ₂ C(NO ₂) ₂ CH ₂ O] ₂ CF ₃	348.2		18	1.51		- 253		
FPFO [FCH ₂ C(NO ₂) ₂ CH ₂ O] ₂ CH ₂	348.2		41	1.63		- 253		
NPMFF [CH ₂ C(NF ₂) ₂ CH ₂ O] ₂ CH ₂	336.21	67(0.15)		1.45	0.025	- 177	1.06	
NPDF [CH ₂ C(NF ₂) ₂ CH ₂ O] ₂ CF ₃	379.19	48(0.15)		1.51	0.020	- 269	0.95	
<u>Ethers</u>								
FEDEE [FC(NO ₂) ₂ CH ₂ O] ₂ CH ₂ CH ₂	334.2	118(0.01)	30	1.54	5.2 x 10 ⁻³	- 235	1.26	4.09
HTD [FC(NO ₂) ₂ CH ₂ O] ₂ CF ₃ CF ₃	406.1		34	1.68	6.1 x 10 ⁻⁴	- 421	1.05	5.40
<u>Nitrate Esters</u>								
EN CH ₃ CH ₂ ONO ₂	91.07	86(760)		1.10	64	- 47	1.12	
FEN FCH ₂ CH ₂ ONO ₂	109.06	127(760)		1.33	7.6	- 93	1.24	
TFEN CF ₃ CH ₂ ONO ₂	145.05	66(760)		1.48	150	- 185	0.86	
<u>Nitroskanes</u>								
DNE CH ₃ CH(NO ₂) ₂	120.07	55(4)		1.35	0.56	- 41	1.34	
FDN CH ₂ CF(NO ₂) ₂	138.06	55(35)		1.41	9	- 87	1.09	
FDNEF FCH ₂ CF(NO ₂) ₂	156.06	39(30)		1.55	17	- 133	1.02	
<u>Nitramines</u>								
ETN CH ₃ CH ₂ N(NO ₂)CH ₂ C(NO ₂) ₂	253.15		64	1.66		- 50		
TFETN CF ₃ CH ₂ N(NO ₂)CH ₂ C(NO ₂) ₂	307.12		59	1.86		- 189		

Bis(trinitroethyl) carbonate was prepared in 71% yield based on the procedure of T. N. Hall²¹ and the carbonate was fluorinated in 87% yield to give the difluoroformal, TEDFO. Our initial attempts to fluorinate the carbonate using sulfur tetrafluoride²² with hydrofluoric acid as a solvent and catalyst resulted in either no reaction or decomposition (Table 6). When the correct reaction time and temperature were used, as in Run 5, a 75% conversion to the desired product was obtained. The reaction temperature and time are critical. Often, the optimum temperature range for sulfur tetrafluoride reactions is only 5°. When the reaction scale was increased to 180 g of carbonate, six days were required to complete the reaction at 105°C. A total of 390 g (232 ml) of TEDFO was prepared for card gap tests.

Bis(fluorodinitroethoxy) Ethane (BFDEE)

BFDEE was prepared by the previously reported^{23,24} procedure shown by the following equations:



Results of running the first two reactions in the sequence were essentially the same as reported in references 23 and 24; however, some difficulty was encountered in obtaining a pure product from the third step. The product (BFDEE) reported in the literature was obtained in 78% yield and of sufficient purity to crystallize on cooling. BFDEE was prepared several times in our laboratory, but yields were approximately 45%, and we found it necessary to chromatograph the product to purify it. These difficulties may have been due to mixing or mass transfer problems because of the

Table 6

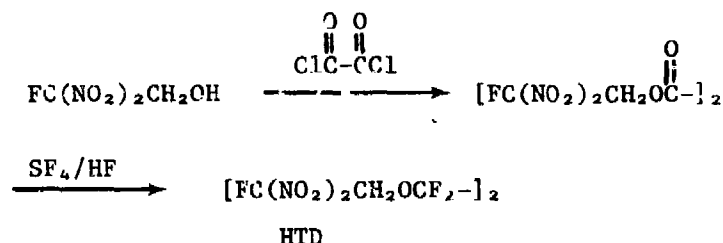
FLUORINATION OF BIS(TRINITROETHYL) CARBONATE

Run	Carbonate (g/mmole)	HF (mmole)	SF ₄ (mmole)	Temp. (°C)	Time (hr)	Product (g)	Remarks
1	10/48	100	157	90	20	9.5	Starting material recovered
2	10/48	1100	102	90	20	9.2	Starting material recovered
3	10/48	1300	74	120	20	9.2	Starting material plus small amount of product
4	10/48	1300	102	120	120	0.8	Primarily decomposition
5	10/48	1100	194	105	72	9.4	75% Product, 25% starting material

larger scale of our reactions. Rather than expending undue effort to modify the reported procedure, we accepted the poorer yield and prepared a total of 158 g (100 ml).

Bis(fluorodinitroethoxy) Tetrafluoroethane (HTD)

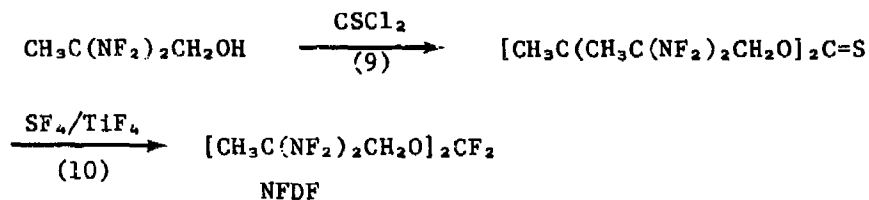
HTD was a known compound²⁵ prepared as shown below.



No difficulties were encountered in the preparation of 140 g (95 ml) of HTD.

Bis[2,2-Bis(Difluoramino)propyl] Difluoroformal (NFDF)

NFDF was the second difluoramino alkyl difluoroformal we attempted to prepare since the formal was already known and 2,2-bis(difluoramino)propanol (a precursor) was already on hand. In view of our unsuccessful attempts to fluorinate bis[5,5-bis(difluoramino)-2,2-dinitrohexyl] carbonate (discussed in a later section), we prepared NFDF using the thionocarbonate, as shown in Equations (9) and (10).



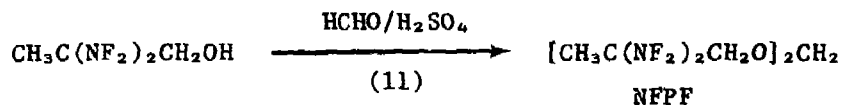
It has been reported²⁶ that thiocarbonates having the general structure RSC(=S)SR can be fluorinated without a catalyst using sulfur tetrafluoride, and in some of our earlier work, a thionocarbonate ROC(=S)OR was fluorinated with sulfur tetrafluoride using titanium tetrafluoride as a catalysts.

The thionocarbonate, Equation (9), was prepared readily from 2,2-bis-(difluoramino) propanol and thiophosgene, and the fluorination proceeded smoothly at 65° in 18 hours to give an 80% conversion.

A total of 20 g of NFDF was prepared, and most of that was consumed in the preliminary sensitivity testing. Because of poor yields in the synthetic route and the hazards involved, we concluded that preparation of sufficient material for shock sensitivity measurements would be prohibitively time-consuming and expensive.

Bis[2,2-Bis(Difluoramino)propyl] Formal (NFPP)

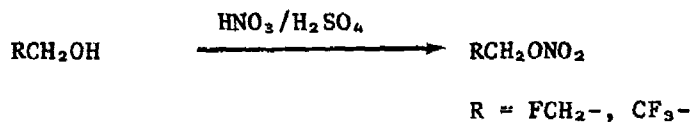
Bis[2,2-bis(difluoramino)propyl]formal (NFPP), the hydrogen analog of NFDF, was prepared according to the following reaction.



The sensitivity hazards encountered in connection with NFDF apply here as well. The poor overall yield of this synthesis is due primarily to difficulties with reaction (11). Success of reaction (11) depends on forcing the equilibrium between the difluoramino alcohol and formal to the product side in sulfuric acid solution. Unfortunately, all the reaction conditions that favor formation of the desired formal also favor decomposition of both the starting alcohol and formal through loss of the difluoramino groups.²⁷ A total of 12 g of NFPP was prepared for preliminary testing, but, as in the case of NFDF, preparation of large quantities required for shock sensitivity testing was prohibitively expensive and time-consuming.

Fluoroethyl Nitrate (FEN) and Trifluoroethyl Nitrate (TFEN)

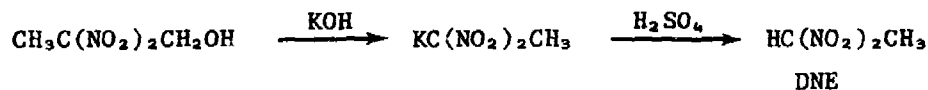
FEN and TFEN were reported in the open literature; however, they were prepared in moderate yields using nitronium tetrafluoroborate. After a brief investigation, we found both FEN and TFEN could be prepared in high yield using a mixture of nitric and sulfuric acids, as shown in the following equation.



A total of 100 g of each of FEN and TFEN was prepared and delivered to LLL for the wedge test after preliminary testing was completed at SRI.

1,1-Dinitroethane (DNE)

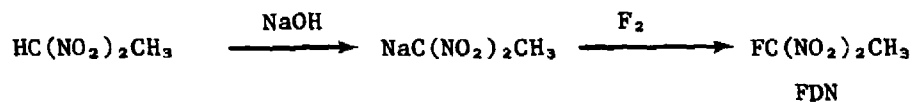
Dinitroethane has been prepared previously²⁸ by oxidative nitration, but for our purposes it was much more convenient to prepare it by deformylation of 2,2-dinitropropanol, as shown below.



We prepared 150 g of DNE for the wedge tests conducted at LLL.

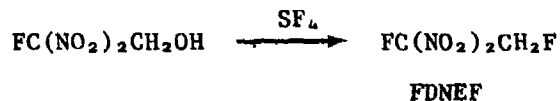
1,1,1-Fluorodinitroethane (FDN)

FDN (150 g) was prepared by fluorination of DNE in aqueous base as previously reported²⁹ according to the following equations,



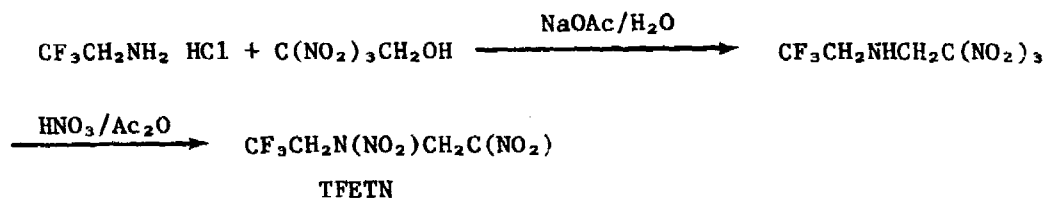
1,2-Difluoro-1,1-Dinitroethane (FDNEF)

FDNEF (90 g) was prepared by fluorination of FDNE with sulfur tetrafluoride as previously reported³⁰ and as shown below.



1,1,1-Trifluoro-3,5,5,5-Tetranitro-3-Azapentane (TFETN)

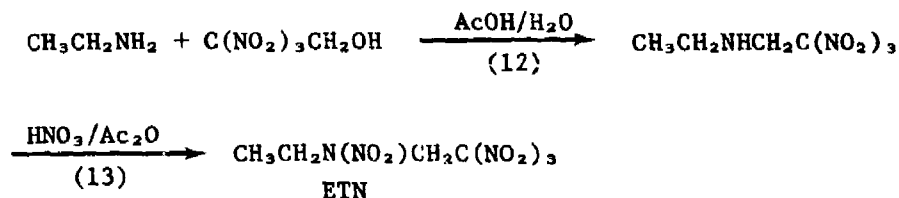
TFETN was prepared by a reported³¹ procedure as shown below.



No problems were encountered using the reported methods, and 150 g was prepared for sensitivity tests

1,1,1,3-Tetranitro-3-Azapentane (ETN)

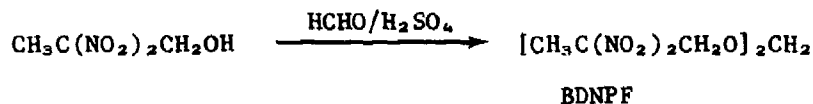
Although ETN is reported in the patent literature,³¹ no experimental details are given for the synthesis. After several unsuccessful attempts to prepare ETN following the same general procedure used to prepare TFETN, we found that reaction (12) yielded the secondary amine in an acetic/water mixture at a pH of 4.1 to 5.1. This was then nitrated to give ETN, Equation (13).



Because of the basicity of ethyl amine and susceptibility of trinitroethanol to deformylation, the pH of the reaction medium is very critical. Further investigation revealed that the highest yields were obtained by slowly titrating an aqueous mixture of trinitroethanol and ethylamine hydrochloride with sodium hydroxide to a pH of 5.1, and then extracting the desired product.

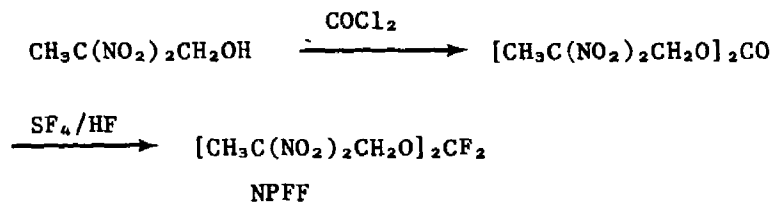
Bis(2,2-Dinitropropyl) Formal (BDNPF)

BDNPF, a well known compound, was prepared as shown below, using the reported procedure³²



Bis(2,2-Dinitropropyl) Difluoroformal (NPFF)

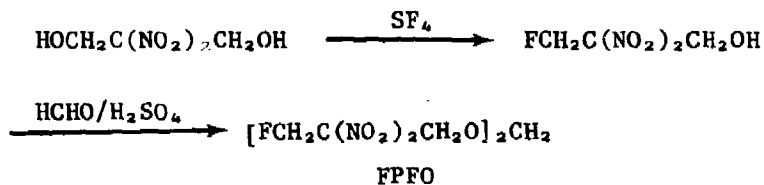
NPFF was prepared under an earlier contract³³ by the following equations.



Preparation of additional material has presented no major problems.

Bis(3-Fluoro-2,2-Dinitropropyl) Formal (FPFO)

FPFO was prepared according to the following equations to compare its sensitivity to BDNPF and NPFF and to determine if the position of fluorine in the molecule affects desensitization.



3-Fluoro-2,2-dinitropropanol, the precursor to FPFO, was previously prepared³⁴ from A-Diol using sulfur tetrafluoride and hydrofluoric acid at high temperature in an autoclave, but the yield was poor (18%). Several attempts to prepare the alcohol in better yield led to the

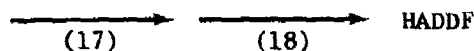
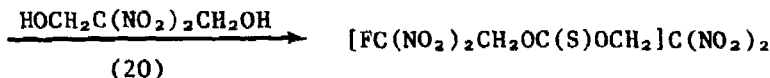
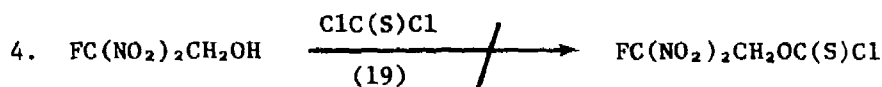
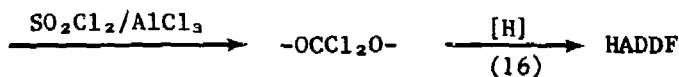
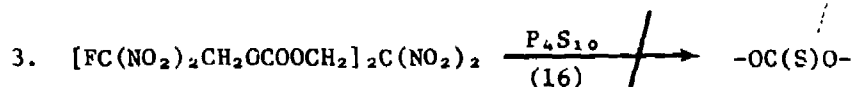
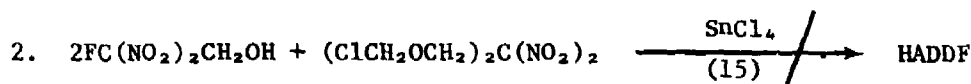
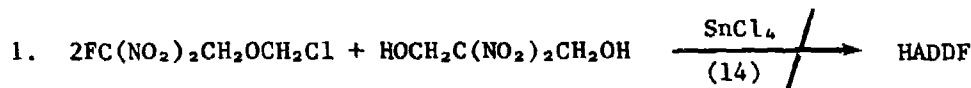
discovery that sulfur tetrafluoride could be used as an effective fluorinating agent at ambient temperature in pyridine-polyhydrogen fluoride reagents. Conversion of the alcohol to the formal presented no difficulties.

In addition to the compounds described above, which were prepared and tested, attempts were made to prepare several other compounds. Although none of the compounds discussed below were prepared, a brief discussion of each is presented for completeness of this report.

1,13-Difluoro-1,1,7,7,13,13-Hexanitro-3,5,9,11-Tetraoxatridecane (HADDF)

HADDF was chosen because the difluoroformal analog, ADDF, was known³³ and had already been shown to be relatively insensitive to initiation. We expected HADDF to be about as sensitive as FEFO and that the ADDF/HADDF pair would therefore provide another pair of formals for which a significant difference in sensitivity could be demonstrated.

In attempts to prepare HADDF, the following synthetic routes were investigated:

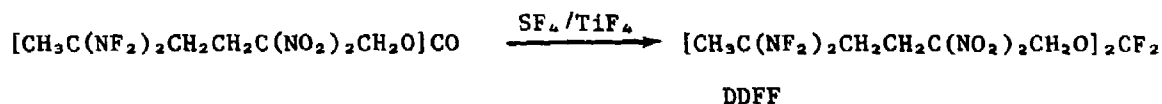


Since the condensation of chloromethyl ethers with acidic alcohols was well known, routes 1 and 2 were attempted first. In both reactions, a mixture of products was obtained in which bis(fluorodinitroethyl) formal and 5,5-dinitro-1,3-dioxane were identified; however, none of the desired product could be isolated.

Attempts to prepare the thionocarbonate, Equation (16), resulted in either no reaction or decomposition of the carbonate. The reaction of fluorodinitroethanol with thiophosgene yielded only the thionocarbonate of FDNE instead of fluorodinitroethyl chlorothioformate, Equation (19). Since it appeared that preparation of HADDF was going to be a difficult problem, the work was discontinued.

Bis[5,5-Bis(difluoramino)-2,2-Dinitrohexyl] Difluoroformal (DDFF)

Since 5,5-bis(difluoramino)-2,2-dinitrohexyl carbonate was available in our laboratories and the formal was already known, we began our study of difluoramino compounds with several attempts to fluorinate the carbonate, as shown below:



Previous work conducted at SRI for Lawrence Livermore Laboratories has shown that carbonates containing the difluoramino group are unstable in the presence of hydrofluoric acid and boron trifluoride, both of which are commonly used as catalysts for sulfur tetrafluoride fluorinations. Therefore, titanium tetrafluoride, which is a milder catalyst, was used in our attempts to prepare DDFF. The results are summarized in Table 7. The reactions, which were run at 120°C, provided a reasonable weight recovery, but spectral data indicated that the product mixture contained mostly starting material. The data also indicated that the desired product was present. When the reaction temperature was increased to 140°, mostly starting material was recovered after one day, and little product at all was recovered after three days. The product from Run 4 contained very little starting material, but the poor weight recovery would make this reaction impractical even if the product mixture were all the desired product.

Table 7

FLUORINATION OF 5,5-BIS(DIFLUORAMINO)-2,2-DINITROHEXYL CARBONATE

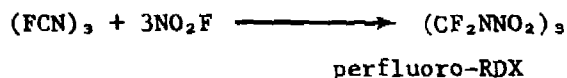
Run	Temp. (°C)	Time (days)	Weight ^a Recovered	Comments
1	120	1	0.4	Mostly starting material
2	120	5	0.3	Mostly starting material
3	140	1	0.3	Mostly starting material
4	140	3	0.1	Little starting material

^a0.5-g scale reactions.

The results of this series of reactions indicated that titanium tetrafluoride was not a very efficient catalyst for fluorination of carbonates. Therefore an alternative approach to the preparation of difluoraminoalkyl difluoroformals was taken, as was discussed in the previous section.

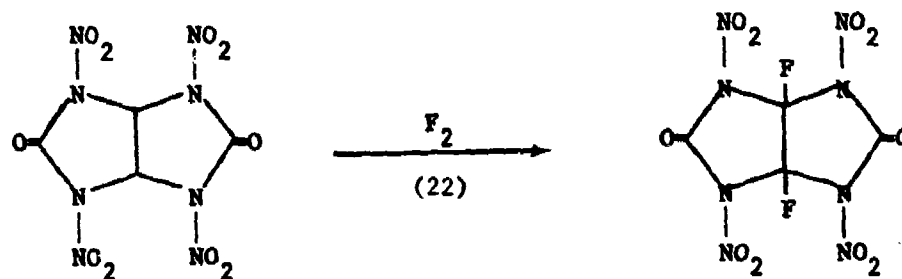
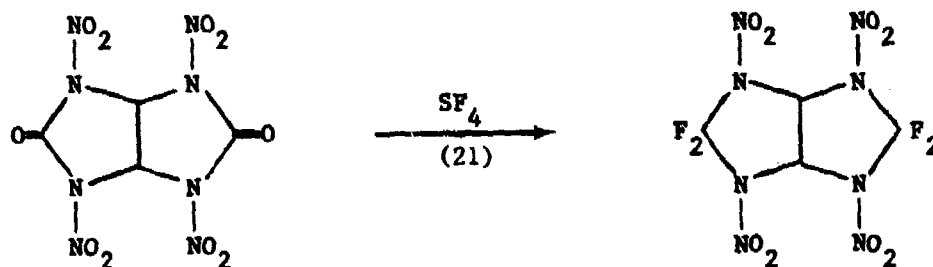
Nitramines

Several attempts were made to prepare fluorinated nitramines. For example, efforts to prepare perfluoro-RDX by the following reaction resulted in an unstable, unidentified product.



Our experimental procedure was based on vague information provided by the reported reaction of cyanuric fluoride with chlorine monofluoride.³⁶ The reaction consumed a theoretical amount of nitryl fluoride to give a product that reacted vigorously with sodium chloride plates and slowly decomposed to volatile products after standing at ambient temperature.

Several attempts were made to fluorinate tetranitroglycoluril (TNGU), Equations (21) and (22), using sulfur tetrafluoride and elemental fluorine, respectively.



The first reaction with sulfur tetrafluoride using titanium tetrafluoride as a catalyst at 100°C gave no reaction, and a second attempt at 120° resulted in detonation of the mixture after a 20-minute reaction time. Work on this reaction was discontinued for safety reasons. We attempted fluorinations with elemental fluorine, (22), using acetonitrile or hydrofluoric acid as a solvent and also as a solid phase reaction by mixing TNGU with sodium fluoride. All resulted in no reaction.

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