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Technical Progress Report 64-4, Quarterly | *June 15 to September 14, 1964*

SENSITIVITY FUNDAMENTALS (U)

Prepared for:

OFFICE OF NAVAL RESEARCH
DEPARTMENT OF THE NAVY
WASHINGTON 25, D.C.

CONTRACT NO. Nonr 3760(00)

SPONSORED BY ARPA-PROPELLANTS CHEMISTRY OFFICE
ARPA ORDER NO. 301, AMENDMENT NO. 3

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

[redacted]

ARPA Cont. No. 11251

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SRI

November 6, 1964

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By: A. B. AMSTER M. W. EVANS M. E. HILL T. MILL

SRI Project PRU-4051

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ABSTRACT

The donor-attenuator system used in the shock sensitivity measurements has been calibrated in the region, 70-150 kbars. The effect of the continuous wire upon apparent sensitivity has been studied: whereas the sensitivity of 1,2-DP appears to be independent of wire length, that of nitromethane is not. A method is suggested and used for avoiding this difficulty.

The sensitivity of 1,2-DP is independent of diameter for diameters more than twice the failure diameter.

Revised sensitivity values are reported. These are based on the new calibration and are for samples of "large" diameter tested to minimize the effect of the sensor. The results follow:

Nitromethane	114 ± 6 kbars
1,2-DP	99 ± 6 kbars
2,2-DP	110 ± 6 kbars
IBA	106 ± 6 kbars

The uncertainty reflects imprecision in the attenuator calibration, not in the raw test results.

Low velocity waves of ~1.8 mm/μsec have been produced in 90% nitromethane -10% tetranitromethane mixtures.

Transit time measurements have been made on 1,2-DP contained in smooth-bore holes in lead blocks. At diameters below 2 mm a very low velocity regime has been encountered whose properties differ in some respects from those studied by other investigators in less unusual materials. From the safety point of view it is disturbing to note that low velocity waves can be started at low shock pressures in holes whose diameter is less than 1 mm.

[redacted]

One goal of the program for modifying the JANAF booster test is to develop a detonability test useful at extremes of temperature and pressure. Two methods are being investigated; both measure detonation velocity. A modified Dautriche method, using explosive witnesses, has been found accurate to ±10%. A continuous-wire oscilloscopic method is accurate to ±5% and can more readily distinguish stable from unstable shocks. Both methods have been found useful at cryogenic temperatures, and provision has been made for using either method in conjunction with a specially designed test vessel.

Evidence has been obtained that base-promoted elimination of HF from 1,2-DP proceeds by a concerted removal of HF from the molecule, in contrast to a mechanism involving reversible carbanion formation followed by NF bond cleavage. In acidic aqueous dioxane solutions, titration of liberated fluoride ion gave preliminary first order rate constants of 1.33 and 1.16 x 10^{-4} sec^{-1}. A final procedure is being developed from this system to study the solvent isotope effect in order to establish whether the decomposition is acid-catalyzed.

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I INTRODUCTION

This research program is divided into three major areas:

(a) Detonation studies of liquid difluoroamino compounds

(b) An experimental and theoretical study of the relation of shock sensitivity and failure diameter to the flow and chemical reaction rate behind the shock front

(c) The mechanism and kinetics of thermal decomposition of difluoroamino compounds.

The detonation studies include (1) measurement of the shock sensitivity of the difluoroamino compounds of interest; (2) determination of whether or not the compounds exhibit low-order detonation and, if so, the necessary conditions for initiation; (3) modification of the JANAF sensitivity test so that it will be more meaningful and more adaptable to conditions of extreme temperature and pressure.

The objectives of the physics and chemistry of detonation, (b) above, are (1) to demonstrate the steady detonation of difluoroamino compounds; (2) to establish failure diameters of difluoroamino compounds in metals and other materials; (3) to study events in the liquids as shocks of various magnitudes enter; (4) to study, where possible, the Chapman-Jouguet velocity, the equation of state of the unreacted materials, and the divergence of the reactive material in the wave.

The study of the kinetics and mechanisms of thermal decomposition of difluoroamino compounds continues along lines previously established and includes a study of the effect of acidic, basic, or neutral additives on their decomposition.

The previous quarterly report* reviewed and discussed the experimental information obtained with respect to thermal stability, detonability, and decomposition kinetics of several bis(difluoroamino)propane isomers and IBA.

This quarterly report reviews the most recent work on the modified JANAF sensitivity test, and the recent results from studies of detonation sensitivity, failure diameter, and decomposition of 1,2- and 2,2-bis-(difluoroamino)propane (1,2- and 2,2-DP) and 1,2-bis(difluoroamino)-2-methyl propane (IBA).

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*SRI Technical Progress Report No. 64-3, Quarterly, "Sensitivity Fundamentals."

II DETONATION SENSITIVITY

(A.B. Amster, D.M. McEachern, Jr.)

A. Shock Sensitivity of Difluoroamino Compounds

Introduction

During this report period the donor-attenuator calibration was extended to higher pressures, experiments were conducted to study and eliminate the effect of the wire sensor upon sensitivity measurements, and measurements were made with 1,2-DP to establish that the test diameter used was sufficiently large to assure that the sensitivity would not be greater for larger diameters. We have also started a series of measurements on standard explosives for comparison purposes.

Donor-Attenuator Calibration

Sensitivities measured for the NF_2 compounds are in the range 90-110 kbars (see below) but the donor-attenuator system used for these measurements had been calibrated for pressures below 40 kbars.[1] To satisfy the need for high pressure data the experimental arrangement shown in Fig. 1 was used. Concentric, circular, diffusely reflecting mirrors of diameters decreasing with distance from the donor are placed at known locations by preparing the mirrors on the polished surfaces of Plexiglas cylinders of precisely known thicknesses and arranging them as shown.

The mirrors are photographed by a smear camera with its slit aligned perpendicularly to the longitudinal axis of the cylinder (Fig. 1-b). A sudden change in mirror reflectivity signals the arrival of the shock, and from a typical record (Fig. 2) one can calculate the position-time behavior of the wave.

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[1] Technical Progress Report 64-2, Annual, March 15, 1963 to March 14, 1964.

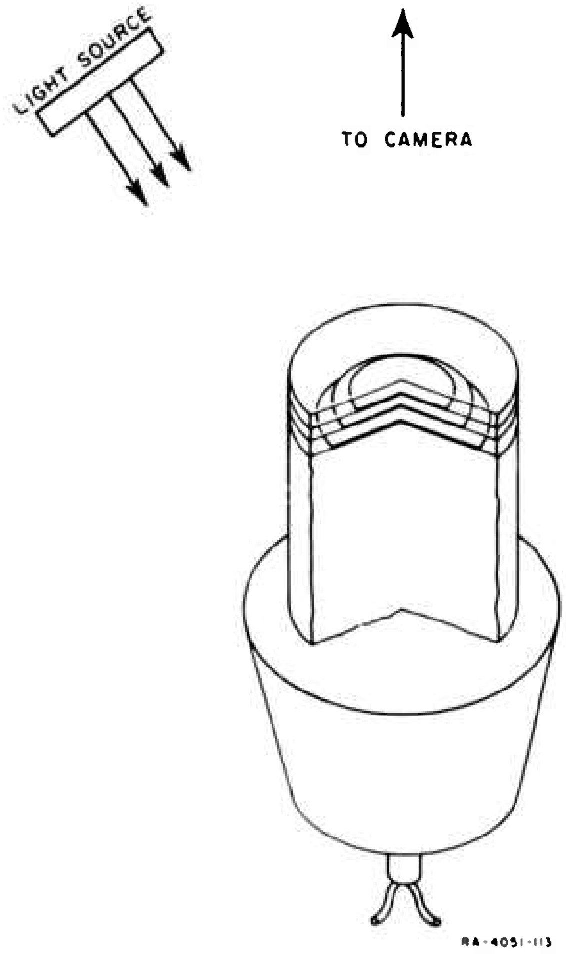

FIG. 1 METHOD FOR MEASURING SHOCK VELOCITY IN LUCITE — SCHEMATIC

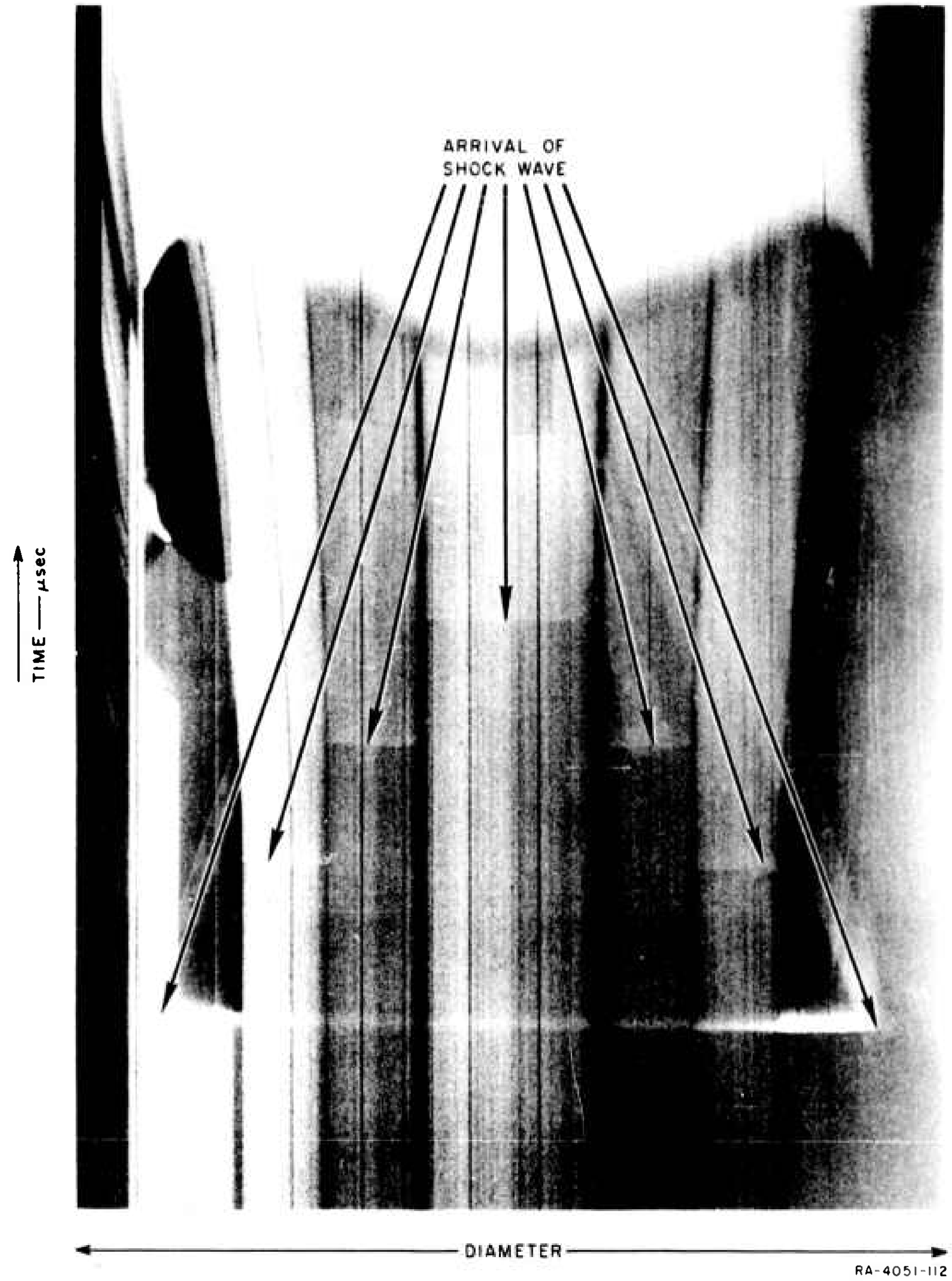

FIG. 2 TYPICAL CAMERA RECORD — USE OF MIRRORS FOR MEASURING SHOCK VELOCITY IN LUCITE

The data are fitted to a quadratic equation using a least squares treatment. Differentiation of the equation gives the velocity-distance relation, and pressure is calculated, as before, from the equation of state.

The averaged results of four separate experiments are plotted as triangles in Fig. 3 together with previously reported data. The vertical lines in Fig. 3 on the two low pressure curves represent the limits of precision of the calibration in that range and are calculated from the results of a large number of shots performed using two tetryl pellets as the donor. The assumption is made that, though pressure is donor-dependent, the precision is equally representative of all-tetryl and combination PWG-tetryl donors. The vertical lines on the high pressure curve are calculated from the spread in the results for the separate experiments. This spread has been found to be larger than any imprecision in a single experiment.

Fortunately, the over-all precision improves rapidly with pressure, from ~50% at 15 kbars to 10% at 65 kbars and 6% at 160 kbars. Approximately 3.5% (in P) is attributable to uncertainty in the velocity.[1] The temperature dependence of the equation of state of Plexiglas introduces an insignificant error[2] at ambient temperature (~0.1 kbar/°C).

We conclude therefore that the major source of error is in the irreproducibility of the donor components.

Effect of Wire Sensor Upon Apparent Sensitivity

The wire sensor method is convenient when other techniques are incompatible with the tested system. The sensitivity, however, may itself be affected by the presence of the wire. A way was sought to detect such a dependence of sensitivity on wire presence.

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[2] D. Schmidt, unpublished results.

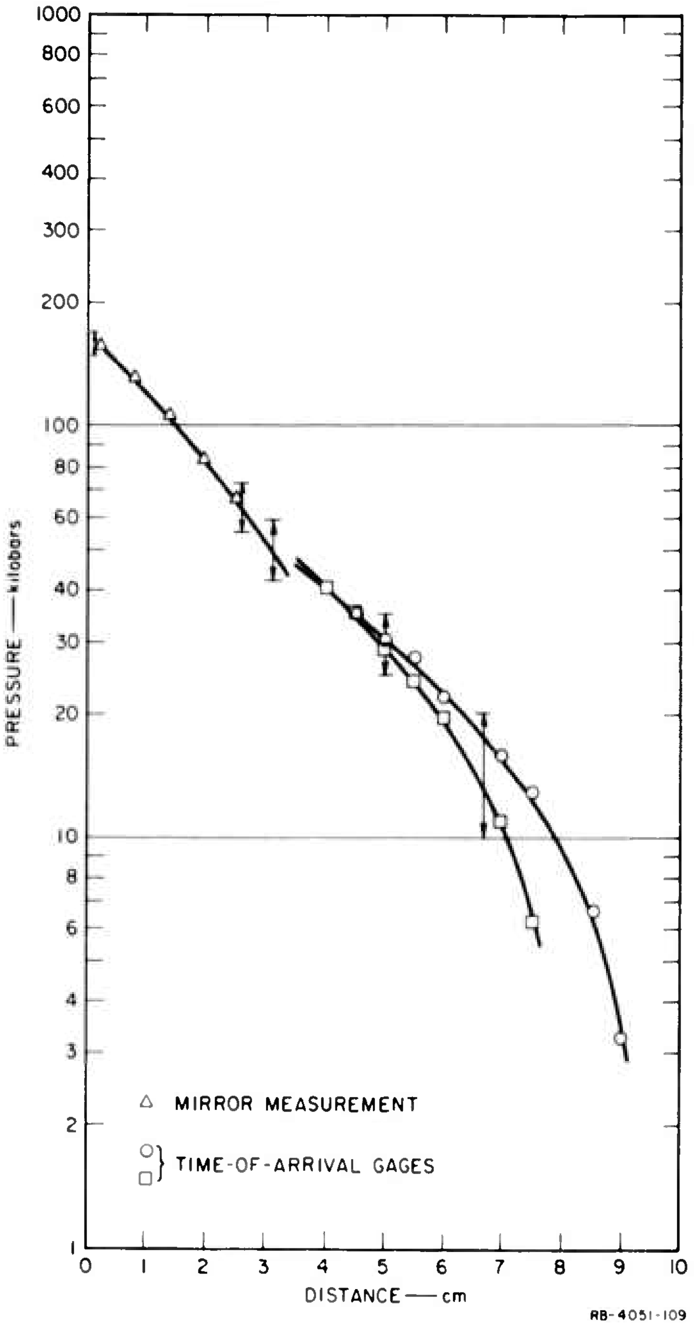


FIG. 3 CALIBRATION OF CARD GAP TEST

The sensitivities of nitromethane and of 1,2-DP were measured using sensors that ran the entire length of the cup and only half way (the half away from the donor). Also, for nitromethane, sensitivity was measured using witness plates. For the 1,2-DP the results were independent of wire length. The nitromethane results (Table I) indicate that, within the precision of measurement, the half-length wire and the witness plate give the same result which differs significantly from that using the full length wire. The relatively simple shock in the liquid is transformed, when it interacts with the sensor (as with any inhomogeneity), to produce a quite complicated pattern of reflections, reinforcements, etc. The effect of this transformation is to amplify the effect of the normal shock wave. Thus a 96-kbar incident shock reaching the full length wire (practically at the attenuator-liquid interface) is as effective as a 112-kbar shock in the absence of a sensor, an effect of less than 20%.

Table I

EFFECT OF SENSOR UPON APPARENT SENSITIVITY

Liquid: Nitromethane
Confinement: Lead cups, 25.4 mm I.D. x 3.1 mm wall x 100 mm long
Donor: PWG + 1 tetryl pellet

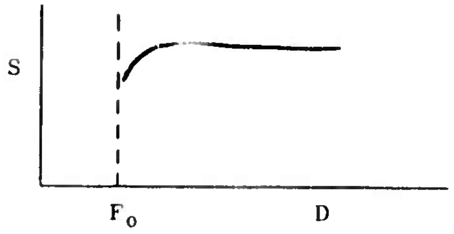
Sensor	Sensitivity	
	Attenuator (inch)	P (kbars)
Full-length wire	$0.63_5 \pm .01_5$	96
Half-length wire	$0.46_5 \pm .01_5$	118
Witness Plate	$0.47_5 \pm .01_5$	112

Two inches of liquid will generally attenuate a shock by 50% or more. For example, assuming that nitromethane and Plexiglas are of similar impedance (a fair approximation) a 112-kbar shock will have attenuated to approximately 30 kbars after 50 mm of travel to meet a half-length sensor. From the results it is apparent that the effects of a 30-kbar wave interacting with the sensor are not sufficient to initiate detonation.

In truth, the extension of these results to the general case is not completely justified. Consider, for example, a low-velocity wave, such as reported by Van Dolah and others. Even at a considerable distance from the shock source such a wave might undergo a transition to a high velocity detonation upon interacting with an inhomogeneity. However, Mason reports[3] several experiments in which wire sensors have been tested as detectors of low velocity waves. In no case has the wire caused a transition to a high velocity wave. We have repeated these experiments with similar results. Therefore, although conclusive proof is not yet available, we feel that sensitivity tests conducted with a "half-length" sensor give valid results. Hereafter all sensitivities obtained using a wire will be obtained with the short sensor.

Effect of Diameter Upon Sensitivity

It is often assumed that sensitivity, S, increases with charge diameter, D, as shown in the following sketch



Above some diameter (generally ≈1-1/2 times F_D, failure diameter) sensitivity is approximately independent of diameter and has a maximum value. The sensitivities we have measured have, in all cases, been measured at diameters $D > 1\text{-}1/2\ F_D$. To confirm that the choice of test diameter is consistent with the goal (for safety) of reporting the maximum sensitivity we have repeated tests on 1,2-DP using other diameters. The results are summarized in Table II where the average deviations arise from having run a minimum of tests to conserve material, rather than from

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[3] C. Mason, U.S. Bureau of Mines, private communication.

contradictions in results. The results are essentially consistent with each other and we are assured that the requirement for testing at a sufficiently large diameter has been met for the 1,2-DP. Test diameters chosen for 2,2-DP and IBA were selected using the same criteria as for 1,2-DP and we assume the results are equally valid.

Table II

EFFECT OF CHARGE DIAMETER UPON SENSITIVITY

Compound: 1,2-DP
Confinement: Lead cups
Donor: PWG + 1 tetryl pellet
Sensor: "1/2 length" CRISP wire sensor

Cup Dimensions (mm)			Sensitivity
I.D.	Wall	Length	Attenuator (mm)
10	2	100	15.9 ± .6
19	2	100	15.3 ± 1.0
24.5	2-3	100	16.1 ± .4
			Average = 15.8 ± .3

Corrected Values for Sensitivities of NF_2 Liquids

Assured that sensitivity tests were conducted a) with sensors which do not affect results and b) at the proper diameters, and with a more reliable donor-acceptor calibration, we report in Table III the sensitivities of the compounds studied.

Table III

LIQUID SENSITIVITIES

Liquid	Sensitivity	
	Attenuator (mm)	P(kbars)
Nitromethane	11.1 ± 0.8	114 ± 6
1,2-DP	15.8 ± 0.6	99 ± 6
2,2-DP	13.2 ± 0.5	110 ± 6
IBA	14.4 ± 0.2	106 ± 6

The liquids all have sensitivities easily distinguishable in terms of attenuator thickness but overlapping in terms of pressure. This is because of the uncertainty in the pressure-gap thickness calibration. Inasmuch as this is attributed to irreproducibility of the shock donors, one would expect the uncertainty to appear in both methods for reporting sensitivity. This anomalous reproducibility of card gap results is perplexing and raises a question we are unable to answer at this time.

Tests with Other Explosives

To establish a frame of reference against which the sensitivities of the NF_2 compounds can be evaluated we will conduct tests with a number of standard explosives. Of these we have already tested nitromethane (sensitivity = 114 ± 6 kbars) and tetryl (30 ± 5 kbars). We propose to measure cast Composition B and other materials as they become available.

Future Plans

The program to characterize the sensitivity of the three liquids is almost completed. We intend to measure the sensitivities of several other materials for comparison purposes and to compare the two donor systems (PWG-tetryl and two tetryl pellets). The comparison of the donors will be expressed both in terms of velocity of shock in the attenuator and of measured sensitivity of several explosive acceptors. The former measures only pressure, the latter is, as yet, an ill-defined function of the pressure-time profile.

Recalling our earlier experiences in which anomalous results were obtained, we intend to study one selected NF_2 compound in glass to establish the effect, if any, of this confinement upon sensitivity.

Lastly, we intend to measure the sensitivity of 1,3-DP when it becomes available.

B. Low Velocity Reaction Waves

In preparation for studying low velocity, low amplitude reaction waves in 1,2-DP, 2,2-DP, and IBA, such as those reported elsewhere in this report (Section III), a series of shots using mixtures of nitromethane and tetranitromethane were conducted. The shots used two types of sensors--the CRISP apparatus and a manganin wire pressure transducer. The experimental geometry was the same as for the sensitivity tests except that thicker plexiglas attenuation (50 mm) and heavy-walled steel tubes were used. With the CRISP apparatus ionization in the wave was not sufficient to produce a record, but by observing the irregularity in the oscillograph caused when the shock entered the tube and when the wire broke an approximate velocity of 1.9 mm/μsec for 90% NM: 10% TNM was observed. The manganin wire pressure transducer registered ~16 kbar during these preliminary investigations. Similarly, velocities of ~1.7 mm/μsec were observed. Damage to the 1/4-inch-thick steel tubes produced by this low order phenomenon is apparent in Fig. 4 where a 12-inch undamaged tube and several fragments from different shots are presented. Similar fragments have been observed to travel 1000 feet and penetrate 2 inches of plywood at 200 feet.

Thus we have established that in a NM-TNM mixture low velocity, low pressure waves are initiated and propagate for at least 12 inches under conditions for which stable, high velocity detonations are not initiated. Further, the damage caused by these explosions is considerable and may be comparable to that accompanying conventional detonations.

Future Plans

We plan additional experiments with mixtures of nitromethane and tetranitromethane using manganin pressure sensors. Framing camera pictures will be taken using rectangular sample containers with clear plastic sides. After methods for observing low order detonations are judged reliable, we will attempt to initiate and to study the low velocity phenomenon in the NF compounds.

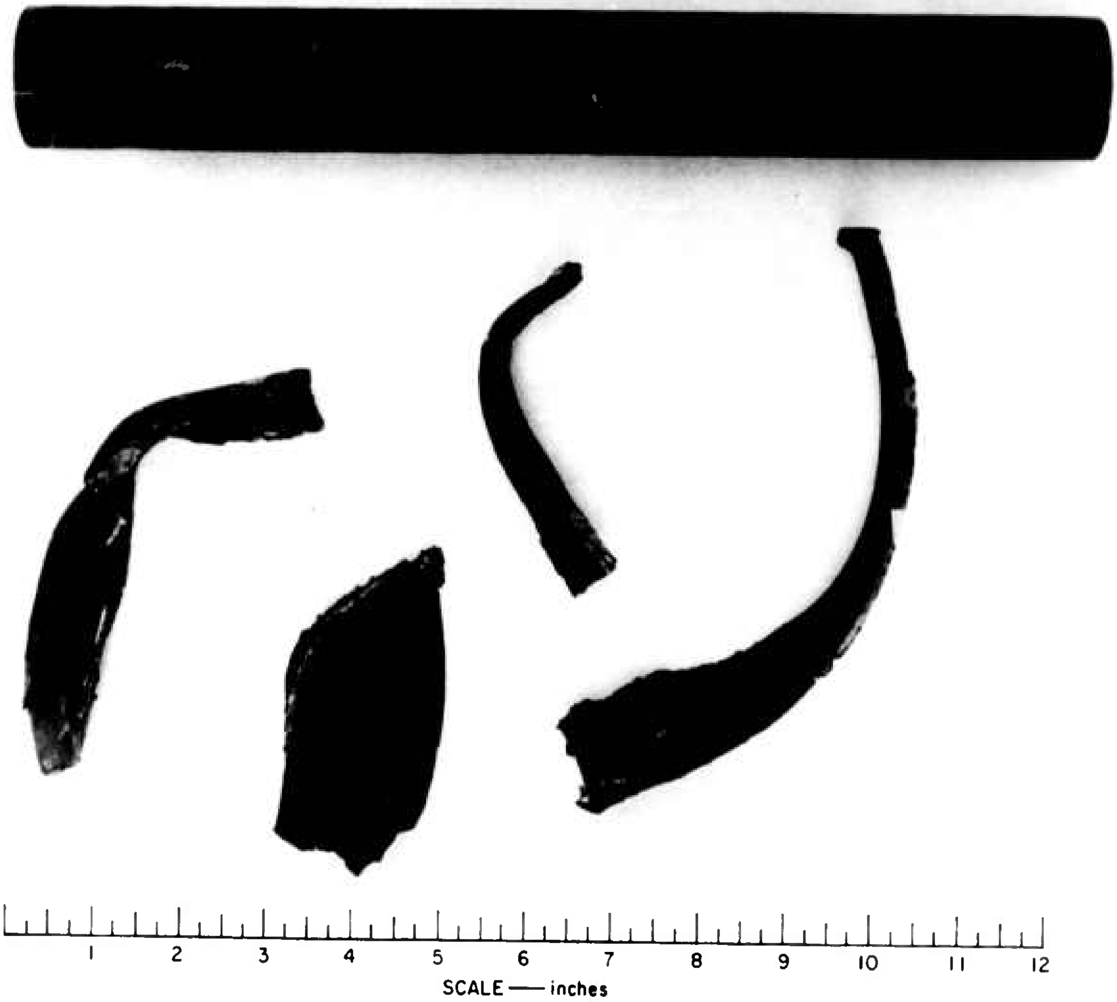

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FIG. 4 LOW VELOCITY DETONATIONS — TUBE FRAGMENTS AND UNUSED STEEL TUBE

III ADAPTATION OF THE JANAF BOOSTER TEST

(A.B. Amster, D.B. Moore, J. Neff)

A. Introduction

The previous quarterly report described two convenient, reliable methods for monitoring strong shocks and detonation velocity in liquids. The first technique utilizes a resistance wire and constant current power supply to yield a continuous detonation velocity record on an oscilloscope. The second, a modified Dautriche technique, utilizes terminal observation of the dents in an aluminum plate caused by explosive witnesses.

The program this quarter has had the following goals:

1. To measure the precision of the Dautriche method
2. To test the method at cryogenic temperatures
3. To design a test vessel for use at cryogenic temperatures and high pressures.

B. Experimental Program

1. Precision of Modified Dautriche Technique

Tests were conducted using Composition B and nitromethane at ambient temperature to test the precision of the explosive witness technique. Results (Table IV) may be compared with reported values of 6.25 mm/μsec for nitromethane[4] and 7.93 mm/μsec for Composition B.[5]

All of the measurements on Composition B lie within 5% of both the reported value and the average of our measurements. The comparable figure for nitromethane is 10% for all but one of the measurements; for the

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[4] A.W. Campbell, W.C. Davis, and J.R. Travis, Phys. Fluids 4, 498 (1961).

[5] M.E. Malin, A.W. Campbell, and Mautz, J. Appl. Phys. 28, 63 (1957).

Table IV

EXPLOSIVE WITNESS DETONATION VELOCITY MEASUREMENTS

Shot No.	Explosive	Velocity (mm/µsec)					
		Explosive Witness Stations					Average
		1-2	2-3	3-4	4-5	5-6	
11	Composition B	6.9	7.9	7.1			7.3
43		6.0	8.4	9.6	6.0	7.4	7.5
44		8.4	6.0	8.8	7.7	8.6	7.9
50		7.4	7.0	7.4	10.7	7.8	8.1
							Mean = 7.7
25	Nitromethane	5.5	5.3	5.7			5.5
30		6.1	6.1	5.7	5.4		5.8
33		6.6	5.3	4.0	12.3	5.3	6.7
34		4.1	9.5	6.6	4.3	8.0	6.5
40L		7.3	5.7	5.7	6.7	7.3	6.5
40R		7.6	5.1	6.1	6.7	7.3	6.6
							Mean = 6.3

exception the difference is 15%. Thus under ambient conditions this method may be considered accurate to within ±10%.

No reliable values have been reported for the detonation velocity of either of these materials at 77°K (b.p. of liquid N_2). Our results are presented in Table V where the value for Composition B is consistent

Table V

TESTS AT 77°K

Shot No.	Explosive	Velocity (mm/µsec) Stations					Average
		1-2	2-3	3-4	4-5	5-6	
45	Composition B	6.6	8.6	7.0	8.6	7.4	7.6
23	Nitromethane	4.8	6.0	6.7			5.8
26		5.9	5.8	6.0			5.9
28		7.5	6.2	7.2	6.1	6.3	6.7
							Mean = 6.1

with an extrapolation from values presented by Malin et al.[5] Our values for nitromethane are all within 10% of the average. Thus at low temperatures, too, this explosive witness method may be considered reliable to within 10%.

Since the test must distinguish between propagation and failure, the results of tests on inert materials are important (Table VI). They indicate that tests on nondetonable systems will not give spurious results.

Table VI

INERT MATERIALS TESTED AT 77°K

Test No.	Material	Results Velocity (mm/μsec) Stations				Remarks
		1-2	2-3	3-4	4-5	
24	Trichloroethylene	2.52	--	--	--	no record after Station 2
47	Liquid Nitrogen	--	--	--	--	no record
48	Liquid Nitrogen	--	--	--	--	no record
49	Liquid Nitrogen	--	--	--	--	no record

The precision of the method depends upon many factors including the care with which the components are aligned and the measurements made. The reproducibility with which the Primacord is initiated by a detonation is also important and at 77°K might prove troublesome. Experiments to initiate several pieces of Primacord simultaneously confirmed that the delay is small enough to have no significant effect upon the measurements.

In summary, experiments have shown that the modified Dautriche method is reliable at ambient temperature and at 77°K, that velocity measurements are precise to ten percent and that results readily distinguish between detonating and nondetonating test substances.

2. Cryogenic Test Vessel and Transfer System Design

The aims of this program include developing a test useful with materials which are gaseous at ambient temperature and pressure. Thus the handling system must have provision for converting a gas, probably at a high pressure, to a liquid--say at 77°K--and the quantity condensed should be just sufficient to fill the test cup. There should be some reliable method for disconnecting the cryogenic section from the high pressure reservoir to prevent reaction propagation from the cup to the storage tank. In addition, system components should be compatible with a wide variety of reactive, sensitive chemicals. Our present design shown schematically in Fig. 5 meets these requirements.

The sample material is normally stored in the gas storage bottle. The measuring bottle is selected to contain conveniently an amount of the gas, at a selected pressure lower than that in the storage bottle, just sufficient to fill the test cell when condensed. Operation is as follows:

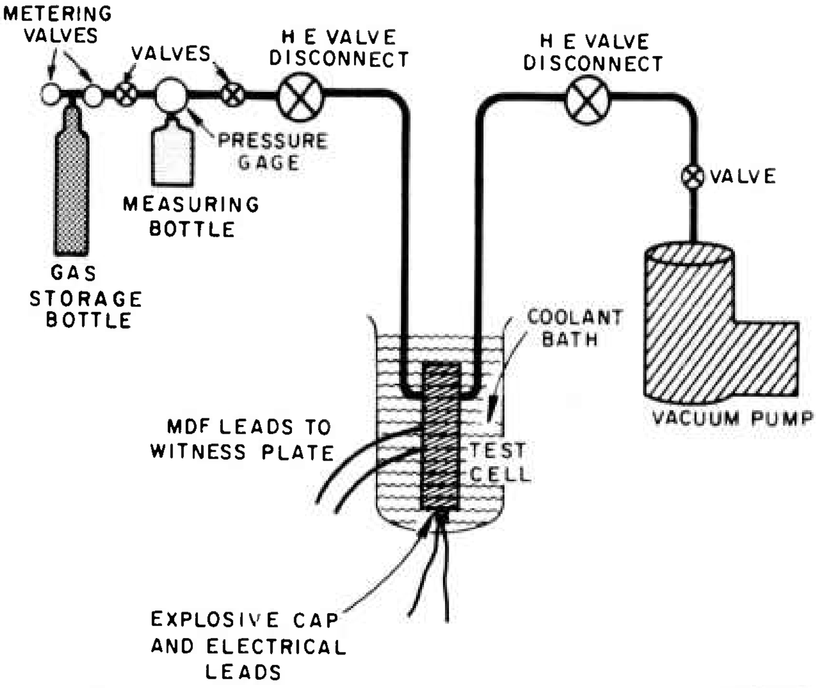

FIG. 5 CRYOGENIC TRANSFER SYSTEM

To start, the entire system except for the storage bottle is evacuated. The pump is disconnected by a valve and the measuring bottle is filled to the desired pressure. The storage bottle metering valve is closed, the test cell refrigerated, and the gas condensed into the cell. When the pressure stops dropping, completeness of condensation is assured. The high explosive valves are actuated to seal the lines as well as disconnect them and then the sample is initiated. Measurements are made with either of the two available methods.

Details of the test cup are shown in Fig. 6. A 0.002-inch stainless steel diaphragm is silver soldered to the bottom of the cup. The top of the cup is fitted with copper tubes and a top cap, both silver-soldered. The tubes are for sample manipulation, and the cap is fitted with electrical connectors to be used (as shown) with the CRISP instrumentation and temperature sensors if desired. An acrylic cap is used at the bottom to retain the tetryl booster. The coefficients of thermal expansion of the plastic, tetryl, and metal are such that, when the unit is cooled to 77°K, the booster is held firmly against the diaphragm.

The unit can be completely assembled before use and kept until needed (with or without explosive components). It is a simple matter to connect the cup to the remainder of the transfer system using compression fittings.

We have considered the problem of determining when the sample cup is filled with liquid. There have been many methods conceived for monitoring liquid levels. The most obvious such as floats, and sight glasses are impractical for our use because of the need for a closed pressurized system which can be completely immersed in a cold temperature bath. Nuclear absorption or reflection devices, electrical and acoustical resonance systems, and the remaining semi-mechanical devices that have been used or proposed tend to be either relatively expensive for one-shot useage, or require an experienced electronic technician to operate, thus defeating the major goal of our effort. In short, there do not seem to be any simple level detectors.

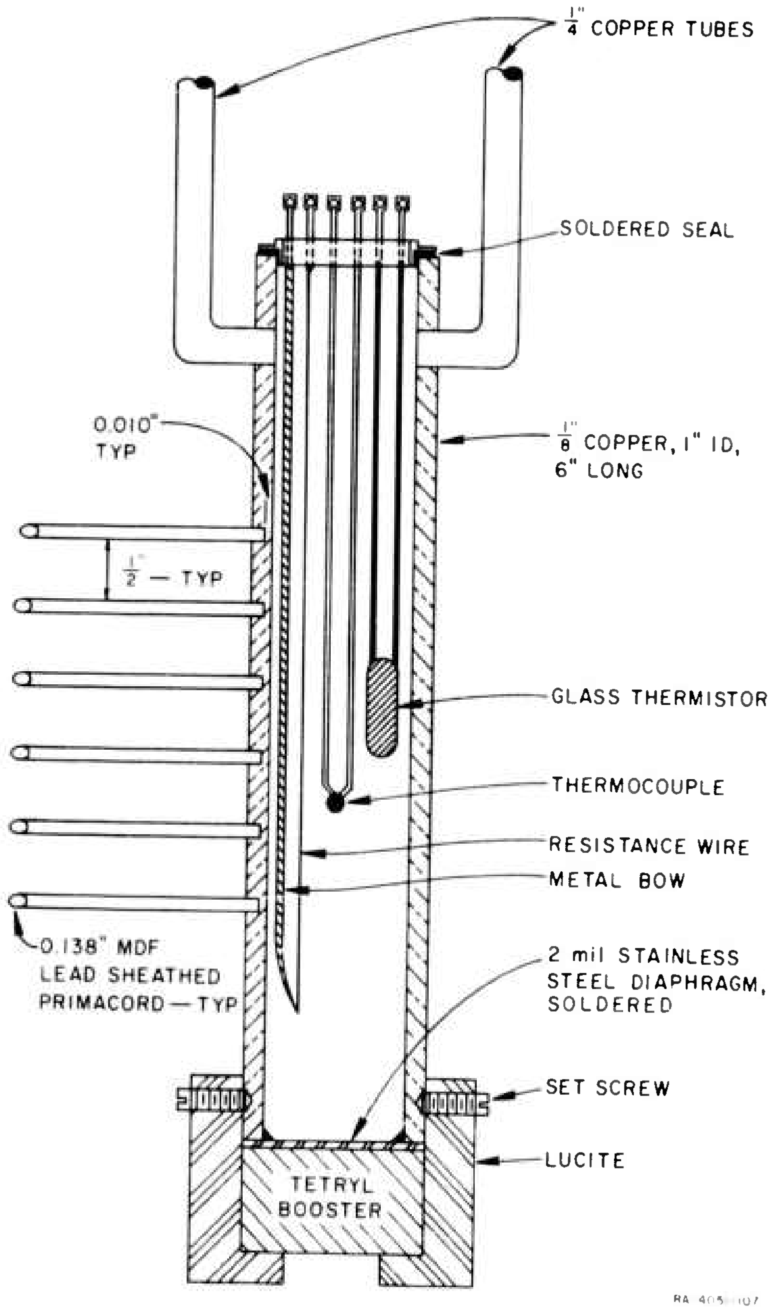

FIG. 6 CRYOGENIC TEST CUP DESIGN

We have developed a thermistor device, described in Appendix A, to establish when the liquid has reached a preselected level. Although it is inexpensive to build and simple to use, and the thermistor can be considered expendable, we feel that the volumetric transfer, described above, is even simpler and more reliable. There may, however, be occasions when the thermistor will be required--and both methods may often be used.

C. Discussion and Future Work

Both the resistance wire technique and the explosive probes are operating successfully. There are some possible difficulties or objections to both systems. We have attempted to anticipate as many as possible. In some situations, the resistance wire and support may affect the behavior of the test material, e.g., the material may appear more sensitive than it is. Our experience indicates that if the wire is never closer than 2 inches from the booster the effect is not detectable.

The explosive probe system perturbs the test sample less but relies on accurate, reproducible assembly and behavior of high explosive materials when handled in the field by relatively inexperienced personnel and when detonated at a variety of temperatures. Our experience on this project has indicated that this is not a serious problem. The system may be less able to distinguish between stable detonations and those of slowly decaying velocity.

We intend to continue studying these problems, but the major effort during the coming quarter will be directed to testing the sample handling system and the test cell. Experiments will be conducted first with Freon-14, then with more energetic compounds, leading ultimately to N_2F_4.

IV PHYSICS AND CHEMISTRY OF DETONATION

(Leslie B. Seely, Marjorie W. Evans,
A. J. Bartlett, Derek Tegg, and Joseph Berke)

In the last quarterly report incomplete results were given on the failure diameter of 1,2-DP, 2,2-DP, and IBA in smooth-walled massive lead confinement. Attention was directed to the safety implications of disruptive propagation in all three explosives at diameters below 1 mm. Transit time measurements now indicate that the waves called "strong" in the last report are actually low in velocity. The hope of avoiding "strange waves" by overboosting has not been realized. Instead, the present results indicate that weak waves in these liquids are initiated by strong as well as weak shocks if the diameter is sufficiently small. This is contrary to the results of Van Dolah with NG-EGDN and Cavea B 110, for which he reported that the low-velocity regime was induced only by weak boosting and then only at relatively large diameters.[6] It is clear we must concern ourselves with the failure diameter of the low-velocity waves as far as safety is concerned. On the other hand, we must concern ourselves with high velocity waves as far as the existing theory of failure diameter is concerned. Here a considerable amount of experimental work remains to be completed.

Measurement of Transit Times

The arrangement for measuring the transit time in a lead-block test is diagrammed in Fig. 7. The first signal was generated by a discharge between foils placed between the RDX booster and the lead block. The signal at the top of the lead block was generated by breakdown between the block and a bare pin held in an insulating cork. Foils could not be used at the top because it was difficult to load the sensitive liquids

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[6] R. W. Van Dolah et al., Low-Velocity Detonation in Liquid Explosives, International Conference on Sensitivity (London, 1963) Session 1, Article VI, p. 4.

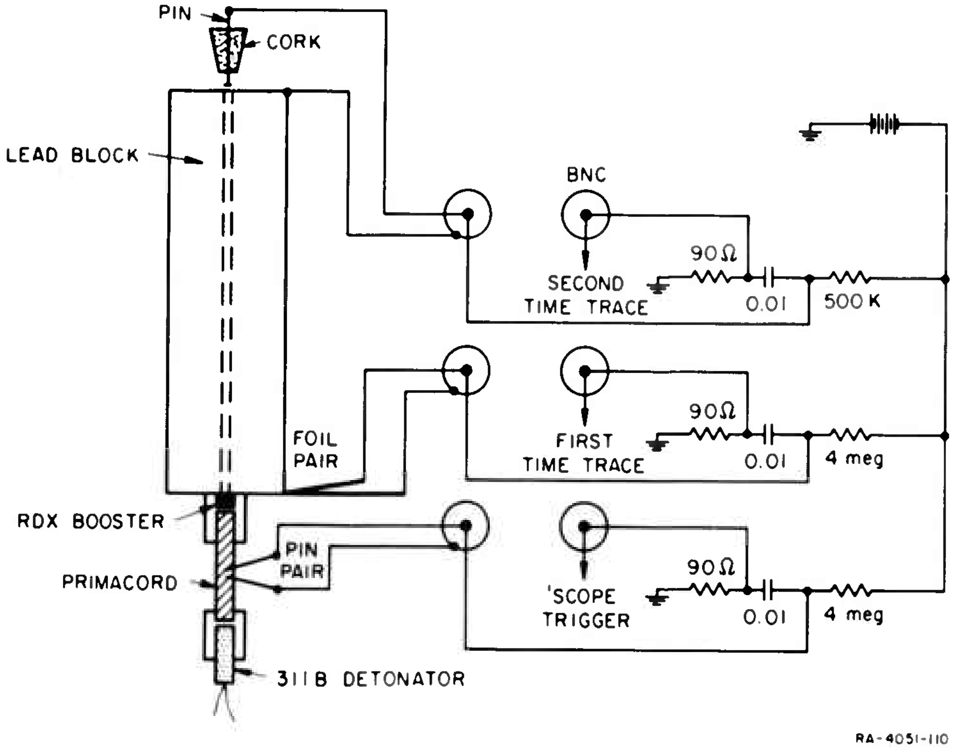


FIG. 7 SCHEMATIC: TRANSIT TIME MEASUREMENT SYSTEM

when foils were taped to the top surface. In order to record the second signal reliably, the voltage was raised from 300 to 600. This resulted in increased conductivity in the liquid and required using the head rather than the point of the pin as the electrode to cut down the field strength. The voltage was maintained in the face of the residual conductance by using a 1/2-Megohm instead of the usual 4-Megohm charging resistor. A typical oscilloscope record is shown in Fig. 8.

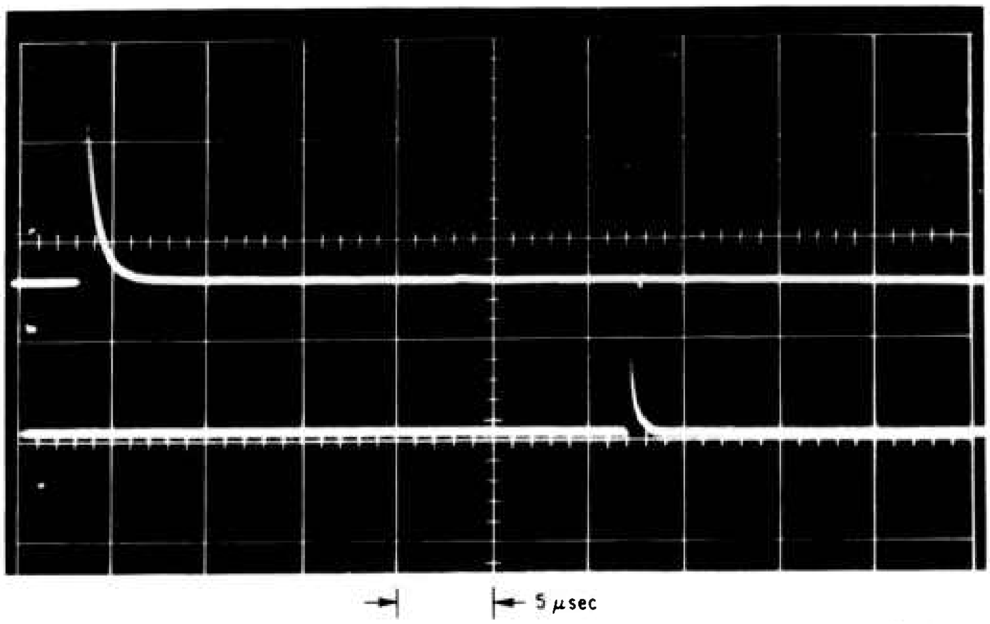


FIG. 8 DUAL-BEAM OSCILLOSCOPE TRACE FROM LEAD-BLOCK TEST
The signal on the upper trace denotes the emergence of the detonation from the booster, the signal on the lower trace the arrival of the reactive wave at the top of the lead block.

1,2-DP

The data so far recorded with this system for 1,2-DP are listed in Table VII. An apparent average velocity (the length of the block divided by the transit time) has been listed in the last column. This number is an average over delays, periods of low velocity, and periods of high velocity. It may not correspond accurately to any quasi-stable velocity. On the other hand it should be a satisfactory basis for distinguishing between waves that could reasonably be associated with the reaction-rate/diameter-effect theory of failure in the range of 5 mm/μsec and much slower waves near 2 mm/μsec.

Table VII

TRANSIT TIME MEASUREMENTS ON 1,2-DP

Booster: 3.1 mm x 3.1 mm Cylinder
of RDX at 1.67 g/cm^3

Shot No.	Hole Diameter mm	Length mm	Time μs	Apparent Average Velocity mm/μs
3	0.8	51.0	38.3	1.33
4	0.8	51.0	37.6	1.35
15	0.8	51.0	32.0	1.59
12	0.8	102.1	88.0	1.16
6	1.6	48.6	27.9	1.74
7	1.6	48.7	28.9	1.69
8	1.6	48.7	28.9	1.69
11	1.6	102.4	64.5	1.59
13	1.6	102.7	67.0	1.53
5	2.1	51.2	8.0	6.4

An indication of local delays and low velocity regions can be obtained by measuring transit times over several lengths. A few 100-mm-lengths have been tested, yielding velocities similar to those in the 50-mm blocks. Measurements on other lengths, particularly shorter lengths, are to be made soon. The transit time measurements can not measure the detailed velocity, and a continuous measurement would be preferable. However, this is practically impossible at these small diameters. Even at somewhat larger diameters it is difficult to measure the instantaneous velocity without producing discontinuities in the wall or introducing inhomogeneities into the body of explosive.

Figure 9 shows a 50-mm-long and a 100-mm-long lead block sectioned after firing. It can be seen that the pattern of the expanded lead in the first 50 mm is repeated in the second 50 mm. Thus the similar apparent average velocities in these two lengths may not indicate a constant velocity in either length, and shots with various other lengths are required to determine the velocity pattern. Cyclic "chuffing" of a low-velocity reaction wave has been noticed by Van Dolah in other materials and is believed by him to occur when the wave is receiving no stabilization from waves in the confining material. It is possible that shock reflections from the outside surface of the lead block may determine where the reinforcement of the wave occurs. Firings with blocks of two different outside diameters are to be made in order to test this.

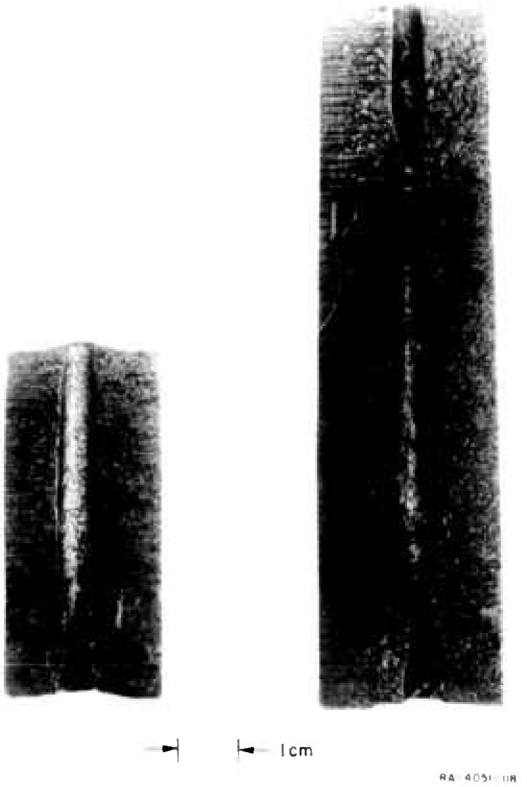


FIG. 9 SECTIONED LEAD BLOCKS AFTER TESTS WITH 1,2-DP. On the left is a block 50 mm long and on the right a block 100 mm long. Both charges were boosted with a 3.1 mm × 3.1 mm RDX pellet at 1.68 g/cm^3. The original diameter of the hole was in both cases 0.8 mm.

The last entry in Table VII shows a high velocity for 1,2-DP in a hole 2.1 mm in diameter. This suggests (although one shot is not reliable evidence) that a high-velocity wave can propagate above this diameter. Additional experiments are being performed to define the relationship between the velocity regimes.

Nitromethane

Lead block failure-diameter tests have also been run on nitromethane to serve as a comparison for less well-known compounds. Nitromethane is less expensive, more available, and easier to work with than the difluoroamino compounds. Eighteen tests have been made in the neighborhood of failure diameter. Some of the charges that fired gave satisfactory timing results and are listed in Table VIII. They differ from 1,2-DP results in the absence of a low-velocity regime. Failures were recorded at both 2.4 and 3.2 mm diameter and for such failures no second pin signal was recorded and the lead block showed no distortion except near the booster. In the case of charges that fired the apparent average velocity was near 6 mm/μsec and the lead was evenly expanded along its entire length. There was no intermediate behavior. Typical expanded lead blocks for 1,2-DP and nitromethane are compared in Fig. 10.

Table VIII

TRANSIT TIME MEASUREMENTS ON NITROMETHANE

Booster: 3.1 mm x 3.1 mm Cylinder
of RDX at 1.67 g/cm^3

Shot No.	Hole Diameter mm	Length mm	Time μs	Apparent Average Velocity mm/μs
5N	2.4	51.7	8.5	6.1
18N	2.4	51.7	8.5	6.1
16N	3.2	51.0	8.1	6.3
17N	3.2	51.0	8.0	6.4

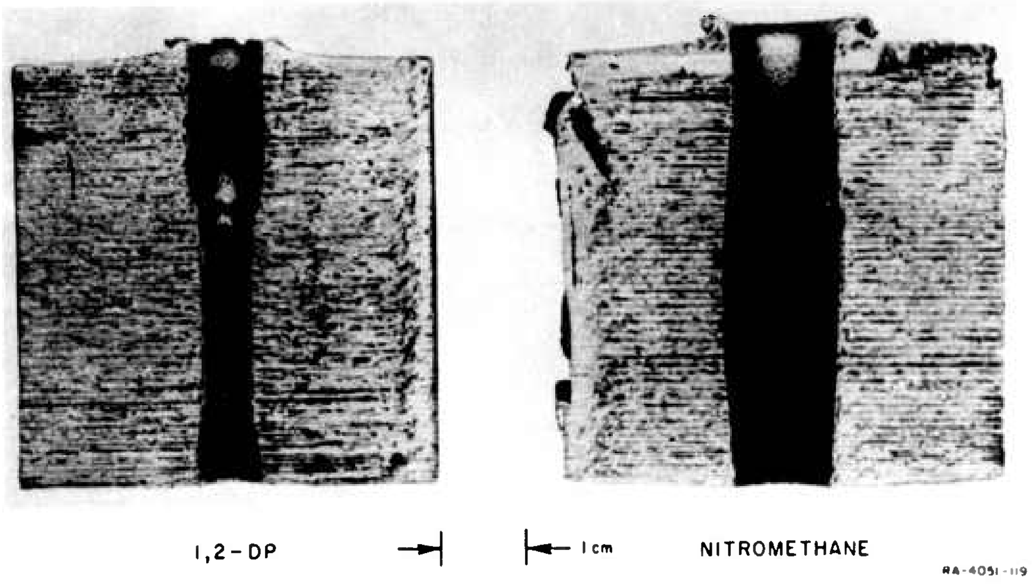


FIG. 10 COMPARISON OF TYPICAL EXPANDED LEAD BLOCKS FROM TEST WITH 1,2-DP (left) AND NITROMETHANE (right). Although the boosters were the same in these shots, the hole in the nitromethane block was 3.2 mm, in the 1.2 DP block 1.6 mm.

Future Work

The diameter range for the full strength detonation and the low velocity modes will be determined for each material in some detail. We expect to be able to measure the velocities in the weak regimes approximately, and perhaps elucidate the transition mechanism. An attempt will be made to estimate the pressure range over which the lowest velocity waves may be initiated.

Now in progress is a measurement of the detonation velocity in 1,2-DP with sufficient accuracy to evaluate assumptions made in detonation calculations. The values previously determined indicate that some revisions should be made, but additional confirmation of these indications is necessary.

Experiments are also being prepared to test the feasibility of determining the reaction time as a function of pressure in an initiating shock. A shot has been fired with a high pressure shock which shows that the transition to the full strength wave can be determined in a head-on view with the smear camera. The next problems to be investigated will be accurate moderation of the shock and determination of the transition time to the full strength wave.

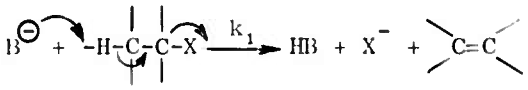
V THERMAL DECOMPOSITION OF NF COMPOUNDS

(T. Mill and D.S. Ross)

Base-Promoted Elimination of HF from 1,2-DP

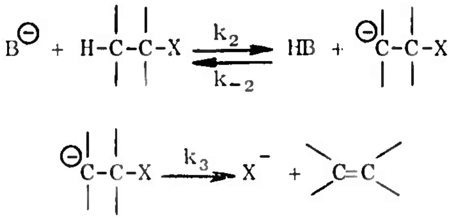
In the last report, the data obtained in the study of a base-promoted elimination of HF from 1,2-DP was not easily interpretable in terms of a well-defined mechanism. Thus, one equivalent of triethylamine appeared to promote the elimination of three equivalents of HF. Further, if the elimination is run with more than one equivalent of triethylamine present, the initially formed N-fluoroiminonitrile disappears slowly, yielding unidentified products.

A systematic investigation into the mechanism of the above elimination reaction is continuing. And, while in this last quarter the majority of the time was spent in a study of acid catalysis of the decomposition (see below), a significant finding concerning the reaction of 1,2-DP with base has been made. Traditionally two mechanistic schemes are put forward for elimination reactions involving a base. First, the so-called E2 mechanism involves a concerted removal of a β-proton by base and heterolysis of the C-X bond.



$$B^{\ominus} + H\text{-}C\text{-}C\text{-}X \xrightarrow{k_1} HB + X^- + {>}C{=}C{<}$$

Second, the so-called E1cB mechanism requires two steps: an initial, reversible carbanion formation, followed by heterolysis of the C-X bond.



$$B^{\ominus} + H\text{-}C\text{-}C\text{-}X \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HB + {}^{\ominus}C\text{-}C\text{-}X$$

$${}^{\ominus}C\text{-}C\text{-}X \xrightarrow{k_3} X^- + {>}C{=}C{<}$$

(Note that the two schemes become kinetically indistinguishable when $k_3 \gg k_{-2}$.) Most elimination reactions are thought to proceed by the first process. However, there are a number of cases reported in which the second scheme is implicated.[7] In these cases strongly electronegative

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[7] J. Hine, R. Wiesboeck, R.G. Shirardelli, J. Am. Chem. Soc., 83, 1219 (1961).

groups present in the molecule facilitate the formation of the carbanion. Since an NF_2 group must be fairly electronegative, the elimination may proceed via the carbanion mechanism.

An experiment was run to determine by which path the base and 1,2-DP reacted. A solution of 0.2 M sodium acetate and 0.055 M 1,2-DP in CH_3OD was allowed to stand at room temperature for 24 hours. (Preliminary work had shown that the conversion to NFP proceeded about halfway in this period.) An examination of the solution by mass spectrometry (a comparison of m/e 94 and 95) subsequently showed no significant incorporation of deuterium in the unreacted 1,2-DP as would be expected were the reaction proceeding via the E1cB mechanism. Thus the initial elimination of HF from 1,2-DP is probably concerted.

Acid-Catalyzed Decomposition of 1,2-DP

The majority of the work carried out this quarter was concerned with the nature of the catalysis in the decomposition of 1,2-DP in the presence of acid. The facts as they stand now (namely the observation of autocatalysis in the decomposition, plus preliminary data on acceleration of the decomposition by HCl) imply either acid catalysis or anionic catalysis or both. It was proposed to run the decomposition in both aqueous HCl and DCl. The ratio of the rates in these two media, k_{H_2O}/k_{D_2O} (the solvent isotope effect), if different from unity, would establish the decomposition as being acid-catalyzed. If k_{H_2O}/k_{D_2O} were unity, while acid catalysis could not be entirely ruled out, the accumulated experimental evidence would thus be consistent with a mechanism involving anionic catalysis. Further experimental procedures could then be brought to bear to establish with certainty the presence of such catalysis.

Several catalysis reactions were studied in order to obtain a solvent-reactant system which would be amenable to kinetic runs. Of the titration systems tried, an acidic aqueous dioxane solution was chosen for further experimentation. Two kinetic runs have been made at 50±0.2° in a medium of 10% dioxane (by volume) and 1.96 M HCl. The reaction was followed (to better than two half-lives) by periodically withdrawing aliquots and titrating (with standard thorium nitrate solution) for liberated fluoride ion. The first-order rate constants obtained, 1.33 x 10^{-4} sec^{-1} and 1.16 x 10^{-4} sec^{-1}, are considered preliminary and more precise runs will be made. (The product in the above runs was NFP. It is stable under these conditions.)

When the final procedure for the kinetic experiments is established, runs will be made in 1.96 M DCl (in dioxane, D_2O). Further possible experiments in this line would involve obtaining rate data in solutions of different acidities, and neutral solutions containing varying concentrations of neutral salts. The above study proposed is of the type routinely used in the study of reactions in strong acid.

Similar experiments are planned with 2,2-DP in order to obtain and identify intermediate decomposition product(s) under mild conditions.

Gas-Phase Decomposition of 1,2-DP

Appendix B contains a report from Rocketdyne Division of North American Aviation describing a series of gas-phase decomposition experiments with 1,2-DP made in a monel, stirred-flow reactor similar to that used for the study of the decomposition of Compound R.* The study was initiated at our request to determine the feasibility of using the flow system technique for obtaining homogeneous decomposition rates at higher temperatures than is possible in the conventional static system.**

As indicated in Appendix B, fairly reproducible rate constants were obtained at the several temperatures between 292 and 501°C where measurements were made. The decomposition appears to be homogeneous in the higher temperature regime, although no specific test for homogeneity such

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*Quarterly Progress Report R 5468-1, Rocketdyne Division PP52-56 August-November 1963. AD No. 345829.

**We thank Dr. Richard Holtzmann, ARPA, and Drs. Houser and Sullivan of Rocketdyne for their cooperation in making this study possible.

as packing was applied. The values for the Arrhenius parameters are reasonable for a unimolecular decomposition. Gas chromatograms of the product and reactant mixtures fail to reveal the presence of significant amounts of intermediates. There is no indication of the presence of NFP assuming that it elutes after 1,2-DP on the Halocarbon oil column. The presence of tars and HF in the reactor system parallels our experience at much lower temperatures in solution and suggests that an HF elimination mechanism is still the important mode of decomposition.

Results of this study give new and more reliable values for the unimolecular decomposition than have heretofore been available; incorporation of the values in failure diameter calculation will be considered later. We plan to examine the behavior of other NF isomers and homologs of 1,2-DP in a flow reactor similar in design to the Rocketdyne device.

Radiation of 1,2-DP

Appendix C describes the results obtained by Shell Development Company laboratories from the radiolysis of 1,2-DP. No evidence was found for dehydrofluorination of 1,2-DP by the ionizing radiation. Instead, elimination of an NF_2 group and fragmentation of the resulting ion accounts for the products observed in the mass spectral analysis.

APPENDIX A

Following is an excerpt of a letter from Dr. J.M. Sullivan, Rocketdyne, reporting their results on the gas phase decomposition of 1,2-DP. The work is also discussed in a report by Rocketdyne, R5468-4, 1 June--31 August, 1964.

"We have investigated the gas phase thermal decomposition of 1,2-DP over the temperature range 292-501°C. The results of our work indicate that in our Monel reactor the reaction is essentially heterogeneous in the lower temperature region and homogeneous above 430°C.

The plot of log k vs. 1/T shown in Fig. A-1 becomes linear at temperatures above 430°C. Least squares analysis of the linear (high temperature) portion of this curve (Figure A-2) indicates that the first order rate constants may be expressed by the Arrhenius equation:

$$k = 10^{16.86 \pm 0.28} \exp(-57{,}300 \pm 900/RT) \text{ sec}^{-1} \tag{1}$$

As you know Atlantic Research Corporation has investigated this reaction in the temperature range 250-350° and found it to be heterogeneous. They report for a glass reactor the Arrhenius equation:

$$k = 2.5 \times 10^{4} \exp(-19{,}000/RT) \text{ sec}^{-1} \tag{2}$$

The results of our work in this lower temperature region are in fair agreement with theirs (the dotted line in Fig. A-1 is given by Equation 2).

Although heterogeneous reactions rates are often difficult to reproduce, we can show that the scatter in our rate constants at the lower temperatures is the result of the relatively small amount of reaction (approximately 15%) which occurred. This situation greatly magnifies the error from the analytical measurements which is 2-3% with this compound. Equation 1 predicts rate constants at 330°C and below which are

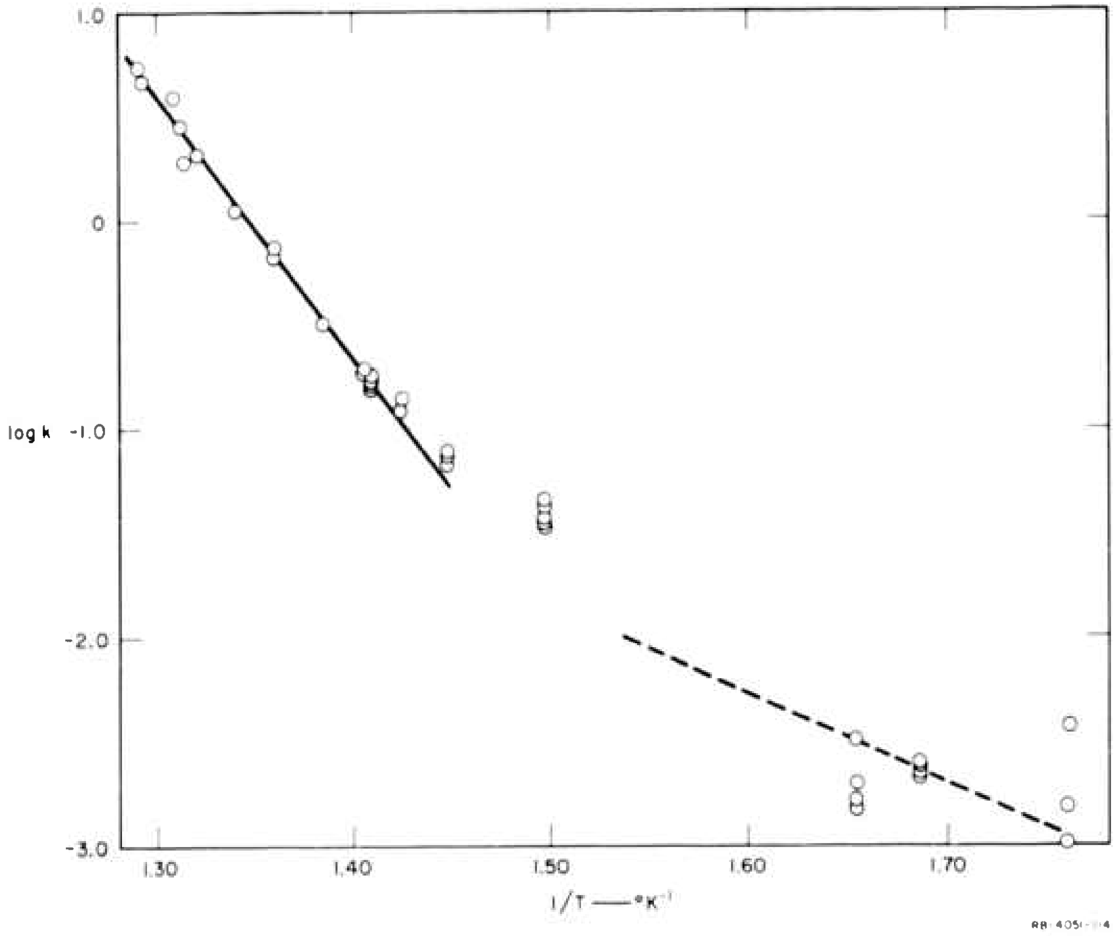

FIG. A-1 ARRHENIUS PLOT OF FIRST ORDER RATE CONSTANTS

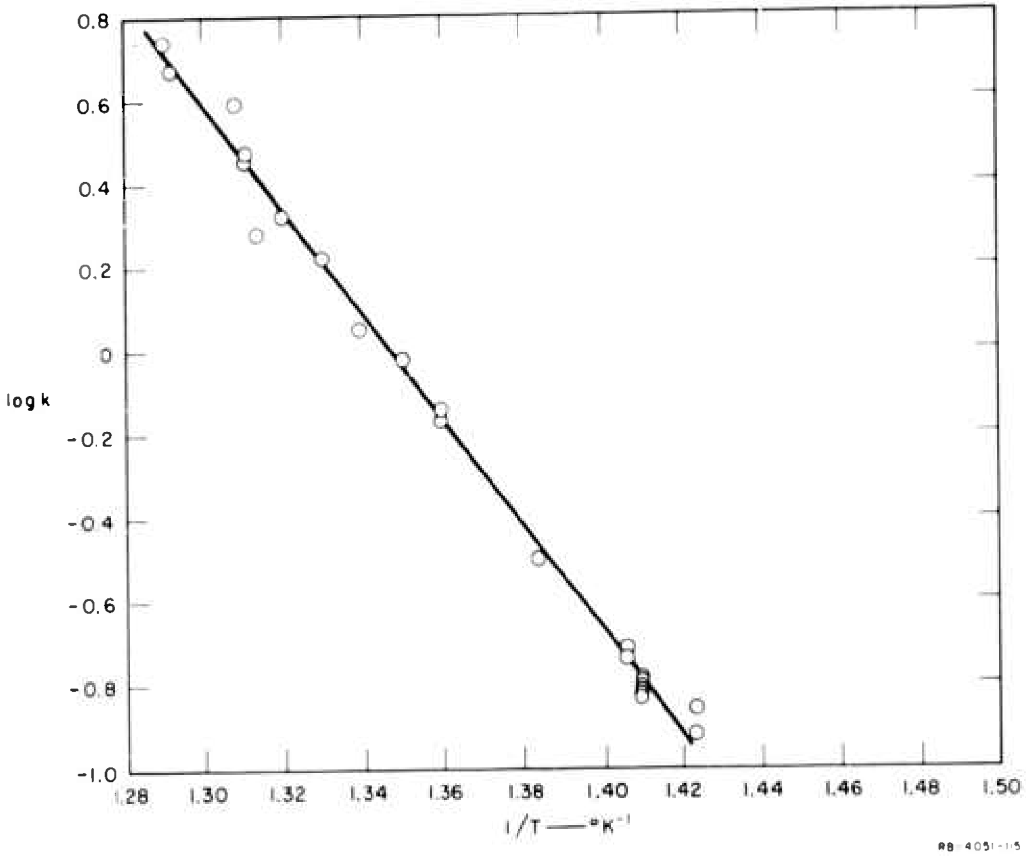

FIG. A-II ARRHENIUS PLOT OF RATE CONSTANTS AT HIGH TEMPERATURE

smaller than the observed values by a factor of twelve or more. We believe, therefore, that we are measuring only the heterogeneous reaction below 330°C and the homogeneous reaction above 430°C. The results at 395°C in Figure A-1 can be explained by postulating that the reaction is 65% heterogeneous and 35% homogeneous at this temperature.

All of our rate measurements were made with a stirred flow reactor, using gas chromatography as the analytical tool. The data obtained are summarized in Table A-I. The total pressure in the reactor was one atmosphere with the partial pressure of 1,2-DP in the reactor varying from 4.7 to 1.2 mm Hg. The remainder was the helium carrier gas. The first order rate constants were calculated from the equation:

$$k_1 = u/v \ (P^o - P)/P$$

where

u = flow rate of the gas

v = volume of the reactor

P^o = peak area of reactant entering the reactor

P = peak area of the reactant from the same size sample of gas leaving the reactor

The first order nature of the homogeneous reaction was determined only at 436°C. The first order plot of these data is shown in Fig. A-3. At higher temperatures, the necessity for high flow rates made it unfeasible to determine the order. By modifying our apparatus slightly, we could obtain some further information on the order of the reaction at these higher temperatures. However, considerable work could be involved and it does not appear that the results would be very meaningful.

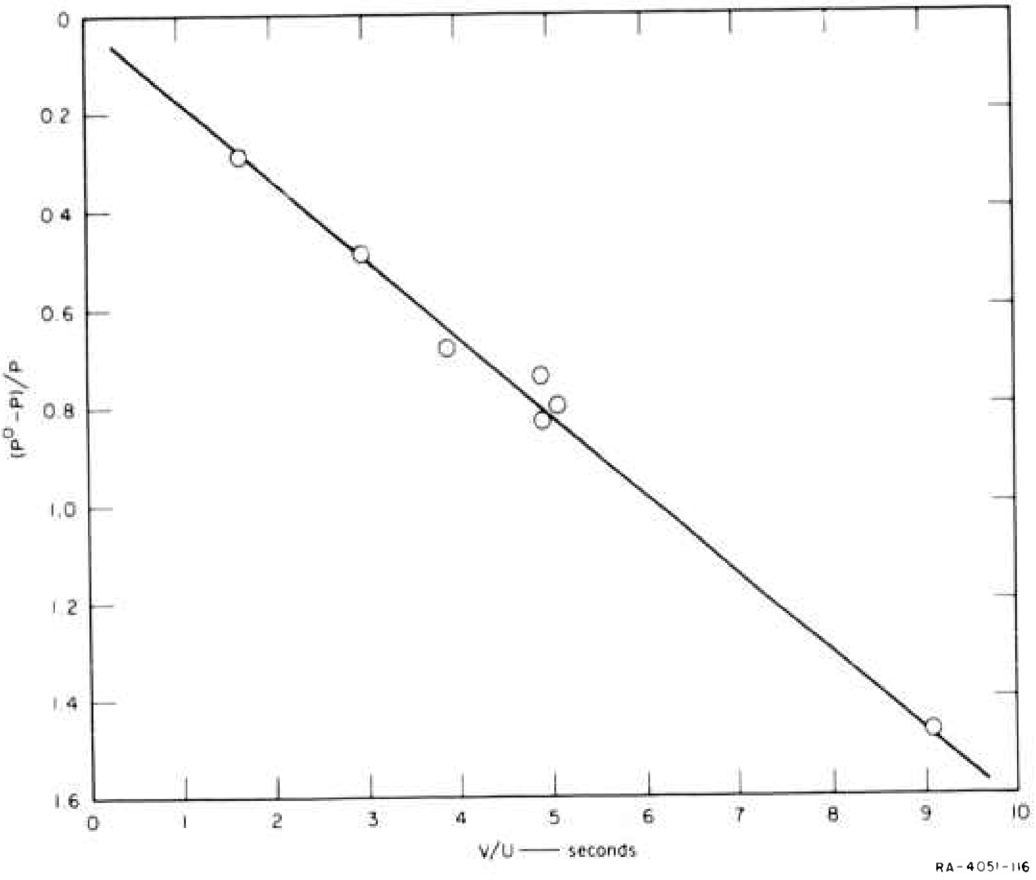

FIG. A-III FIRST ORDER PLOT AT 436°C

No attempt was made to identify the products of this reaction. However, chromatographic behavior and the presence of etching in the glass portion of the apparatus indicated that HF was probably one of the products. Also, we found a brownish black residue in the cold metal tubing leading from the reactor."

Table A-I

DATA FROM GAS PHASE DECOMPOSITION OF 1,2-DP

The following symbols apply to data given in this table:

T = temperature of reactor, ^{o}C.

V = volume of reactor, corrected to reactor temperature, ml.

U = flow rate of gases (1,2-DP and He), ml/sec (at reaction temperature).

C^{o} = partial pressure of 1,2-DP in gas stream, mm Hg (at room temperature).

P^{o} = peak area for 1,2-DP entering reactor, cm^{2}.

P = peak area for 1,2-DP leaving reactor, cm^{2}.

k = first order rate constant, sec^{-1}.

T	V	U	C^{o}	P^{o}	P	k
294.0	152.4	4.330	9.0	429.7	379.7	0.00374
294.2		1.053		436.3	392.0	0.000781
294.4		1.693		465.0	409.0	0.00152
319.8	152.5	1.732	9.0	442.0	363.0	0.00247
320.3		1.628		432.0	361.0	0.00210
320.3		0.906		461.0	343.0	0.00204
320.3		0.652		145.2	92.9	0.00241
490.2	153.8	278.5	3.0	224	87	2.68
487.8	153.8	268.6	3.0	216	103	1.92
484.4	153.7	252.1	3.0	208	91	2.11
478.8	153.7	235.3	3.0	220	105	1.68
473.2	153.7	215.2	3.0	207	114	1.14

Table A-I (Concl'd)

T	V	U	C^o	p^o	p	k
332.0	152.5	4.275	9.0	296.3	265.3	0.00322
332.2		2.613		295.0	264.7	0.00196
332.0		2.245		297.0	267.3	0.00164
332.0		0.741		274.0	213.0	0.00146
417.5	153.3	12.05	9.0	489.3	248.7	0.0755
417.7		28.55		484.0	356.7	0.0686
417.7		22.23		491.0	324.3	0.0731
437.8	153.4	19.95	9.0	526.3	211.4	0.194
438.0		25.20		504.0	236.6	0.186
436.2	153.4	31.2	9.0	506.0	276.8	0.168
436.5		31.2		508.7	293.0	0.150
436.7		30.0		506.7	282.4	0.155
436.7		39.2		506.0	301.4	0.173
436.7		51.6		512.5	345.0	0.163
436.7		92.5		515.3	400.3	0.173
435.8		16.8		535.7	217.4	0.161
462.4	153.6	172.3	8.0	434.0	263.0	0.730
462.4		168.9		422.0	260.0	0.685
449.2	153.5	52.9	8.0	426.0	216.0	0.335
449.2		61.6		412.0	235.0	0.302
428.6	153.3	46.0	8.0	399.0	284.0	0.122
428.8		24.6		423.0	225.0	0.141
395.0	153.1	5.60	8.0	413.0	187.0	0.0442
395.2		11.79		425.0	277.0	0.0411
395.2		8.40		405.0	242.0	0.0370
395.5		13.26		389.0	280.0	0.0337
396.0		9.86		421.0	278.0	0.0331
501.8	153.9	328.5	3.0	421.0	118.0	5.49
501.2		324.4		233.0	72.0	4.72
492.2	153.8	304.7	3.0	229.0	73.0	3.97

APPENDIX B

The following summary is an excerpt from a letter from Dr. J.N. Wilson, Shell Development Company, concerning the study of Dr. R.P. Nielson on the radiolysis of 1,2-DP.

Radiolysis of 1,2-DP

"A 0.15 mole sample was exposed to 180 megarads of 2 to 3 Mev X-rays at -196°C in a thin-walled Monel irradiation tube; the sample was distilled into the irradiation tube from an all-metal vacuum system and frozen at a well-defined location for irradiation. The radiation was generated by the impact of 3 Mev electrons (van de Graaf) on a water-cooled gold target. After irradiation the sample-tube, still at -196°C, was connected to the ionization chamber of a Bendix time-of-flight mass spectrometer. A valve on the sample tube was then opened to connect the sample tube to the vacuum system of the mass spectrometer and any vapors present over the sample at -196° were exhausted through the mass spectrometer; the pumping rate was controlled to keep the pressure in the mass spectrometer in the vicinity of 10^{-6} Torr. The species present in the ionization chamber were monitored by taking their mass spectrum at intervals.

As soon as detectable amounts of material were no longer emitted from the sample at -196°C, its temperature was allowed to rise at a controlled rate. The mass spectrum was monitored frequently by means of an oscilloscope and was recorded at intervals when sufficient signal was generated by the mass spectrometer. In this way the mass spectra of volatile products were obtained as well as information about the temperature required to bring the vapor pressure of that product over the sample into the range 10^{-5} - 10^{-6} Torr. Significant temperatures for the evolution of products from the sample under these conditions were -193, -125, -84, -20, 0 and +45°C.

Some of the products evolved were identified unambiguously from their mass spectra and distillation temperatures; these are NF_3, CH_4, trans N_2F_2, N_2F_4 and N_2. Other products suspected but not identified with certainty because of superposition of mass spectra and the mass-equivalence of N and CH_2 are C_2H_4, CH_2F_2, CH_3F, C_2H_5F and C_3H_6 (n propene). Products that were not detected, though they were sought, are CF_4 and F_2. It is significant that HF was not seen until the distillation temperature reached 65°C; if HF were a primary product of the radiolysis we would expect to see it at a distillation temperature around -90°C. We conclude that the HF seen at 65°C was a product from the thermal or wall-catalyzed decomposition of either the starting material or one of its less volatile irradiation products. A peak with m/q = 18, probably from water, was seen as early as -125°C; its origin is not known but is suspected to be slight leakage of water condensed from the atmosphere on to the cold fittings on the sample tube during the relatively long time that was required for the low-pressure distillation. No other oxygenated species were observed.

The observed product distribution and the failure to observe HF as a primary product imply that elimination of an NF_2 group or some more complex event is much more likely than elimination of HF when this compound is exposed to ionizing radiation. The same conclusion follows from an examination of the mass spectrum of the compound (Table B-I).

Failure to observe the parent ion implies that fragmentation of the molecule is very rapid following ionization; an ion corresponding to the loss of an NF_2 group is observed, however, and this is consistent with the occurrence of N_2F_4 in the products. Secondary fragmentation of this ion could lead to the formation of some of the lighter ions observed in the mass spectrum. An alternative mode of primary decomposition of the parent ion is the formation of N_2F^+ and CH_3-CH-CFH_2; this possibility is one way to account for the very strong 47 peak.

Improvements in technique since this experiment was done would make it possible for us to obtain more quantitative information about the distribution of products; in addition, the identity of some of the products and of the ions in the mass spectrum of the parent compound could be established with considerable certainty by means of our high-resolution mass spectrometer. It appears, however, that the events following ionization of this molecule are complex."

Table B-I

MASS SPECTRUM OF 1,2 COMPOUND

M/q	Possible Ions	Relative Intensity
146	$C_3H_6(NF_2)_2^+$	Absent
94	$C_2H_4N_2F_2^+$, $C_3H_6NF_2^+$	3.9
66	$C_3H_2N_2^+$, $CH_2NF_2^+$	14.2
47	CH_2NF^+, N_2F^+	100.0
42	$C_3H_6^+$, $C_2H_4N^+$,	32.4
41	$C_3H_5^+$; $C_2H_3N^+$	29.5
40	$C_3H_4^+$, $C_2H_2N^+$	12.8
39	$C_3H_3^+$, C_2HN^+	14.8
33	NF^+	15.7
29	$C_2H_5^+$, CH_3N^+	13.7
28	$C_2H_4^+$, CH_2N^+	78.0
27	$C_2H_3^+$, CHN^+	50.5
26	$C_2H_2^+$, CN^+	12.3
15	CH_3^+, NH^+	50.0
14	CH_2^+, N^+	11.8
85	?	2.5
80	?	8.0
75	?	6.7

APPENDIX C

A Thermistor as a Combination Liquid Level and Temperature Sensor

(Donald Baker Moore)

Experiments which involve remote handling of hazardous condensable gases such as modern monopropellants often require temperature monitoring and positive indication that condensed liquids have reached certain container levels. The simplest systems including sight glasses and floats, may be unsuitable because of potential explosion or other personnel hazards. More sophisticated methods, including acoustic or electrical resonance measurements, optical refraction, or nuclear means, may be unnecessarily complex or the probe-sensing element may be too expensive for a potentially expendable system. Such devices also require an additional temperature-measuring probe which is often a thermocouple. A thermocouple alone is frequently inadequate since the saturated vapor and condensate often may be at the same temperature.

A thermistor element such as the VECO 32A11 (Victory Engineering Co., Springfield, New Jersey) is used in this laboratory to combine these measurements with one inexpensive probe. A small, measured direct current in the range of one to ten milliamperes is passed through a thermistor sealed into the experimental chamber at the desired level. The potential drop across the thermistor is measured. This yields both the resistance and power dissipated in the device. The resistance is compared with the thermistor specifications to find the internal temperature of the probe. This temperature is then plotted against the power dissipation figure. A second measurement at a different input current designates a second point on the graph. A straight line through these points intercepts the axis of zero power dissipation at a value corresponding to the temperature of the probe environment. The slope of this line (or its reciprocal) in milliwatts per degree measures the thermal conductivity of the probe environment. This will usually be found to vary by an appreciable factor between the liquid and gas states, and will be characteristic of the sample material.

The illustration shows some test data on this system using Freon 12 as a sample gas. In this case the thermal conductivity changes by nearly a factor of four as the probe environment changes from gas to liquid.

This system is useful at probe temperatures up to 300°C and has been used in liquids at -80°C, although at very low temperatures some care may be required to keep the thermistor's internal temperature above that of its environment to prevent its resistance from becoming impractically large.

The measurements are most conveniently made with a measured or constant current supply and a potentiometric voltage recorder. The thermal time constant for the usual thermistor varies from one or two seconds in a liquid to approximately twenty-five in a gas, so while the indication is not continuous it can be relatively rapid. Obviously, reduction of the observations can be facilitated by suitable graphs.

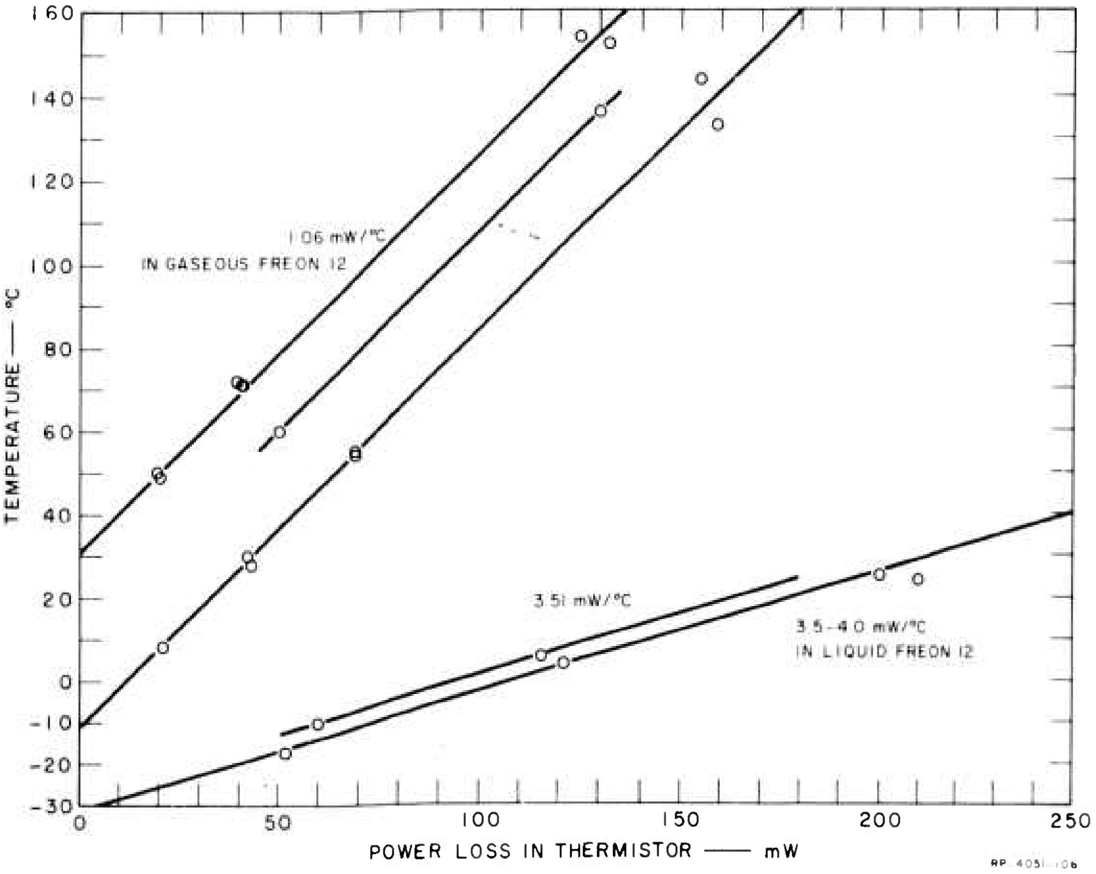

FIG. C-1 POWER LOSS IN THERMISTOR VERSUS TEMPERATURE

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