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Quarterly Technical Report 63-2 | *June 15 to September 14, 1963*

RELATIONSHIP BETWEEN DECOMPOSITION KINETICS AND SENSITIVITY (U)

Prepared for:

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

CONTRACT NO. Nonr 3760

SPONSORED BY ARPA—PROPELLANTS CHEMISTRY OFFICE
ARPA ORDER NO. 301-62

STANFORD RESEARCH INSTITUTE
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By: *A. B. Amster* *M. W. Evans* *M. E. Hill* *T. Mill*

SRI Project No. PRU-4051

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I INTRODUCTION AND SUMMARY

In this report period smear camera observations were made of detonation waves in nitromethane, 1,2-DP, and 2,2-DP. The nitromethane gave essentially conventional results, the detonation wave having a velocity of 6.5-6.7 mm/μsec. Possibly the velocity was still decreasing very slowly 30 cm from the liquid-donor interface. This compares with a steady velocity of 6.3 mm/μsec reported by earlier observers. The 1,2-DP and 2,2-DP, however, again exhibited the anomalous behavior (observed in previous report periods) with continuous wire and pin techniques. The detonation velocity varied from shot to shot: sometimes it appeared steady, sometimes it accelerated, and sometimes it decelerated.

Solutions were obtained for equations which describe a model of three-dimensional, axially symmetric, laminar detonation waves in homogeneous condensed materials. The data are being collected and interpreted.

Consideration was given to the validity of the Halford-Kistiakowsky-Wilson equation of state for product gases in the calculation of ideal Chapman-Jouguet detonation characteristics. A shot was planned in cooperation with Lawrence Radiation Laboratory to give information on the empirical C-J isentrope.

Adiabatic self-heating runs were made on 2,2-DP and IBA. Results from these runs and those made in the previous quarter are reported.

The rate of decomposition of pure 1,2-DP has been measured and compared with calculated values. No kinetic solvent effects were observed in the decomposition of either 1,2-DP or 2,2-DP.

On the basis of elemental analyses and NMR spectra, it has been tentatively concluded that the structure of an intermediate resulting from the decomposition of 1,2-DP is 2-(N-fluoroimino) propionitrile.

II SHOCK SENSITIVITY

(Marjorie W. Evans and A. B. Amster)

A. Experimental

Ten shots were made using the smear camera to observe the detonation wave; three with 1,2-DP, three with 2,2-DP, and four with nitromethane. The geometry of the charges is shown in Fig. 1. The results are given in Tables I-III. (Previously reported No. 28 is included in Table I.)

Anomalies were found similar to those observed in the experiments where detonation velocities were measured electronically.[1] For 1,2-DP, Table I shows that two of the shots (Nos. 109 and 111) did not result in stable velocities. Previously reported No. 28 at the same diameter gave an apparently stable velocity of 6.2 mm/μsec. Shot No. 110 at a larger diameter appeared to give a lower stable velocity of 5.4 mm/μsec.

For 2,2-DP Table II shows one shot (No. 112) in which the wave may be stabilizing at a velocity of 6.4 mm/μsec, and another under apparently identical conditions (No. 113) showing an accelerating wave with an apparent velocity of at least 7.2 mm/μsec. Shot No. 114, at a larger diameter, shows a lower, apparently stable, velocity of 5.0 mm/μsec.

According to Table III, nitromethane displays a more conventional behavior, with a velocity slightly higher than the 6.3 mm/μsec reported elsewhere.[2,3] The velocity appears to be decreasing with distance, even as far as 20 to 30 cm from the donor-liquid surface.

---

[1] "Relationship Between Decomposition Kinetics and Sensitivity (U)," Annual Report, 15 March 1962 - 14 March 1963, Stanford Research Institute Project No. PRU-4051, Contract No. Nonr-3760(00), A.B. Amster, M.W. Evans, M.E. Hill, and T. Mill

[2] G. Nahmani and Y. Manheimer, J. Chem. Phys. 24, 1074 (1956)

[3] J.R. Travis, A.W. Campbell, W.C. Davis, and J.B. Ramsay, "Shock Initiation of Explosives III. Liquid Explosives," Les Ondes de Detonation, Colloques Internationaux du Centre National de la Recherche Scientifique, Gif-sur-Yvette, 1962.

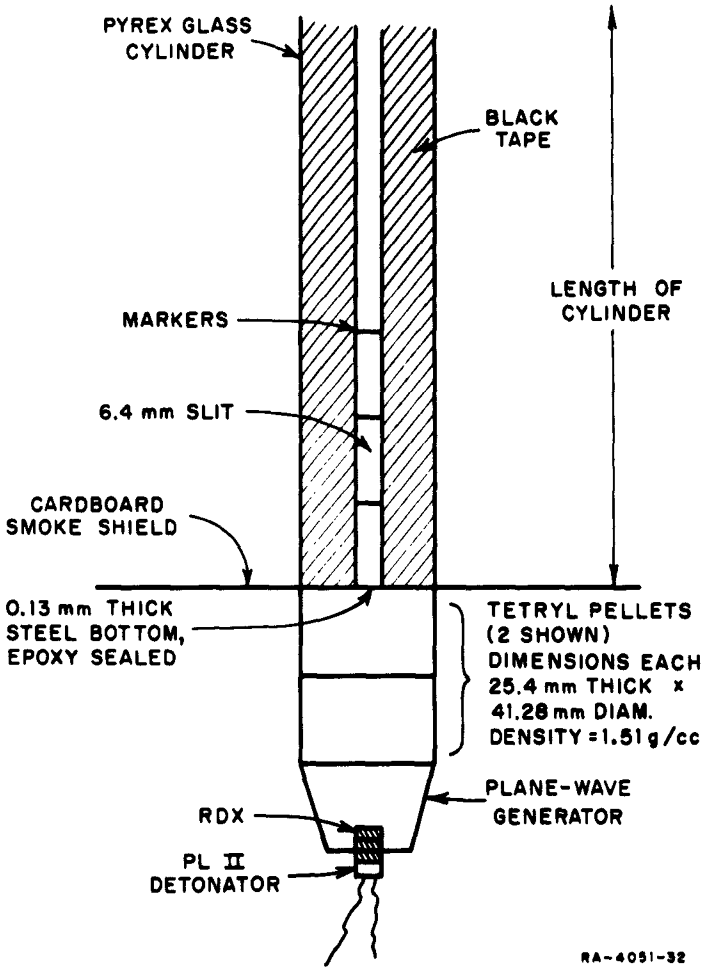

FIG. 1 DETONATION VELOCITY APPARATUS (U)

Table I

Smear Camera Studies of Detonation of 1,2-DP

Shot No.	28	109	111	110
Film No.	9463	9595	9597	9596
Donor:	Plane wave generator and two tetryl boosters			
Acceptor Confinement:	Pyrex glass cylinders			
I. D. (mm)	18.97	18.97	18.97	25.4
Wall thickness (mm)	1.55	1.55	1.55	1.85
Length (mm)	100	100	100	100
Distance from donor-liquid interface (cm)	Detonation Velocity (mm/µsec)			
5	6.2	6.2	6.6	6.4
6	6.2	5.8	6.4	5.7
7	6.2	5.5	6.2	5.4
8	6.2	5.1	6.0	5.4
9	6.2	4.6	5.8	5.4

Table II

Smear Camera Studies of Detonation of 2,2-DP

Shot No.	112	113	114
Film No.	9618	9619	9620
Donor:	Plane wave generator and two tetryl boosters		
Acceptor Confinement:	Pyrex glass cylinders		
I. D. (mm)	12.7	12.7	18.97
Wall thickness (mm)	1.2	1.2	1.55
Length (mm)	100	100	100
Distance from donor-liquid interface (cm)	Detonation Velocity (mm/µsec)		
5	6.7	6.5	5.6
6	6.5	6.4	5.2
7	6.4	6.9	5.1
8	6.4	7.2	5.0
9	6.4	7.2	5.0

In view of this we believe that future experiments with the DP compounds should be done with greater length-to-diameter ratios than those used thus far.

Table III

Smear Camera Studies of Detonation of Nitromethane

Shot No.	105	106	107	108
Film No.	9639	9640	9641	9642
Donor:	Plane wave generator and one tetryl booster			
Acceptor Confinement:	Pyrex glass cylinder			
I. D. (mm)	26.2			
Wall thickness (mm)	1.8			
Length (mm)	300			
	Detonation Velocity (mm/μsec)			
Distance from donor-liquid interface (cm)				
20	6.63	6.68	6.56	6.67
22		6.65	6.53	6.64
24		6.64	6.52	6.61
26		6.62	6.51	6.59
28		6.61	6.51	6.58
30		6.61	6.51	6.57

The apparatus and experimental technique employed in the continuous wire measurements of detonation velocity reported earlier[1] have been carefully re-examined in an attempt to determine if the unusual detonation behavior of the DP compounds can be attributed to measurement technique. The electronic components, individually and combined, have been subjected to detailed examination and performance tests. No malfunction has been detected. Although problems of relating circuit impedance to oscilloscope impedance prevent precise measurements of the wire current during a run, we believe that the potentiometric measurements made immediately prior and subsequent to a shot are reliable. In summary, although the re-examination has not been completed, we are unable thus far to attribute the detonation behavior to peculiarities of the instrumentation.

One pound of 1,2-DP has been furnished to the Chemistry Department of Lawrence Radiation Laboratory, Livermore, California. LRL will perform a shot which, if the material detonates as a conventional Chapman-Jouguet detonation, should give the following information: (1) detonation velocity in a charge 25 mm in diameter, 30 cm long, contained in copper tubing with 2.5-mm-thick walls, initiated with a plane wave lens; (2) an empirical Chapman-Jouguet isentrope which can be compared with that used in the Ruby code calculations of ideal Chapman-Jouguet detonation characteristics.

Detonation is measured with pin rings. The rate of radial expansion of the metal tube behind the detonation front is measured with smear cameras at a selected point along the axis. The complete charge is viewed with a framing camera. From the rate of radial expansion and two-dimensional hydrodynamic theory[4] the empirical C-J isentrope is calculated.

B. Theoretical

Solutions have been obtained of the equations which describe a model for three-dimentional, axially symmetric, laminar detonation waves in homogeneous condensed materials for which the kinetics can be treated formally as a single first-order rate process. The equations were solved for parameter values appropriate for 1,2-DP.

In the absence of experimental data, it was necessary arbitrarily to choose reasonable values for certain parameters and functions. This was done as follows: An unreacted shock Hugoniot was selected which is an average of experimental curves for nitromethane and mononitrotoluene. Extrapolation to high pressure regions was made with a straight line extension of the shock velocity versus material velocity. The Grüneisen ratio was estimated to be a constant and to have a value of 1.25. The Chapman-Jouguet detonation velocity was taken to be 6.55 mm/μsec based on the Ruby code calculation for 1,2-DP.[1] From the

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[4] Mark L. Wilkins and Richard Giroux, "The Calculation of Stress Waves in Solids," UCRL 7271, March 11, 1963.

same calculation, a value of heat of reaction Q for initial state to Chapman-Jouguet state was taken to be 650 cal/g. The initial density was 1.265 g/cc and the heat capacity at constant volume was 0.35 cal/g-cc; these are values obtained by measurement at ordinary temperatures and pressures.

Calculations were run for an initial temperature range of 300 to 450°K, radius of detonation wave curvature to charge diameter ratio of 0.5 and 9, pre-exponential rate factor of 10^{10} to 10^{16} $\sec^{-1}$, and activation energy of 20 to 60 kcal/mole. From the results, failure diameter, detonation velocity as a function of diameter, and shock sensitivity are predictable. Computations have been completed and results are being interpreted.

Initial interpretation suggests that the assumption of a constant heat capacity, independent of temperature and having the value measured at ordinary pressures and temperatures, may be a poor approximation. Consideration will therefore be given to improving the approximation by introducing a temperature-dependent heat capacity, the form of the function being based on the form for similar compounds. Consideration will also be given to the possibility of improving the Grüneisen ratio estimate.

The kinetics of thermal decomposition is not always first order, and has indeed been shown not to be so for 1,2-DP at ordinary pressure and ~200° C.[1] We are therefore exploring the validity of the first order rate approximation for the case where the correct expression has the form which has been found for 1,2-DP,

$$dx/dt = k_1 (A-x) + k_2 (A-x) (x)^2 \tag{1}$$

where A is the original concentration and x is the amount which has decomposed at any given time. Equation (1) is being integrated to give fraction reacted versus time, for the kinetic parameters and original concentrations reported for the low temperature thermal decomposition of 1,2-DP.[1] The time to 99.9% completion for Eq. (1) is being compared with that for the approximation used in the model,

$$dx/dt = k_1 (A-x) \tag{2}$$

as well as with the familiar algebraic approximation[5]

$$t_{\epsilon = 0.999} = (c_v R T_1^2)/\nu E_a Q \exp(E_a/RT_1) \qquad (3)$$

where $t_{\epsilon = 0.999}$ signifies the time to 99.9% completion. Heat capacity is assumed temperature-independent here also.

The validity of this model and these computations rests upon certain major assumptions, as follows:

1. That the Halford-Kistiakowsky-Wilson equation of state which was used in the calculations of ideal Chapman-Jouguet detonation characteristics is appropriate.
2. That the rate law established for thermal decomposition at ordinary temperatures and pressures also applies at pressures and temperatures in the reaction zone of detonation waves.
3. That the detonation wave is a laminar detonation wave with a smooth shock front and with negligible turbulence in and behind the reaction zone.
4. That the assumed relationship between steady detonation velocity and diameter is a good approximation. The equation used in these calculations is the Wood-Kirkwood equation (see Eq. 14 of reference 5).

These are assumptions which call for examination, and in this report period we have considered the first assumption. Although both the Halford-Kistiakowsky-Wilson equation of state[6] and that used by Paterson[7] in detonation calculations are based on theoretical considerations, the justification for their use under the extreme conditions of detonation leaves something to be desired. Rawlinson[8] has developed

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[5] Marjorie W. Evans, J. Chem. Phys. 36, 193 (1962)

[6] See for example: R.D. Cowan and W. Fickett, J. Chem. Phys. 24. 932 (1956)

[7] S. Paterson, Research 1, 221 (1948)

[8] J.S. Rawlinson, "An Equation of State of Gases at High Temperatures," University of Wisconsin, Theoretical Chemistry Institute Report WIS-TCI-32, 15 August 1963

an approximate equation of state based on theoretical arguments and well-defined approximations, the nature of the approximations being such that the equation may be expected to be reasonably valid at high temperatures and high densities. A calculation of Chapman-Jouguet detonation characteristics using this equation of state for the products would make an interesting comparison with the Ruby code calculation already reported, which employs the H-K-W equation of state. Such a calculation is under consideration.

C. Future Plans

The value of using the continuous wire technique for measuring detonation velocities in liquids will be further examined.

A series of smear camera studies of the detonation of 1,2-DP, 2,2-DP and IBA is planned. Present plans call for diameters of 10 and 25 mm and lengths of 30 cm. If detonation occurs at 10 mm diameter, the experiments will be extended to smaller diameters. Shots will be made in both thin-walled and thick-walled Pyrex tubes, in an effort to determine if wall thickness has a measurable influence on the detonation velocity behavior.

It is expected that the two-dimensional hydrodynamic shot of 1,2-DP will be made by Lawrence Radiation Laboratory in the next report period.

Results on the computation of the three-dimensional, axially symmetric, laminar detonation wave will be collected and interpreted. Consideration will be given to introducing a temperature-dependent heat capacity function into the program, as well as to the computation of C-J detonation characteristics using the Rawlinson equation of state for the products. Thought will be given to the problem of determining decomposition rate laws at detonation temperatures and pressures.

III ADIABATIC SELF-HEATING (A. B. Amster)

A. Experimental

In the last quarterly report, preliminary note was taken of one run with 2, 2-DP and of four with IBA. During this report period one additional run was made with IBA and three with nitromethane. In each test a type II bomb with a 0.107 cm wall was used (see reference 1, p. 20). Numerical results are presented in Table IV for these nine runs; the reduced data are plotted in Fig. 2 for the 2, 2-DP, in Fig. 3 for the IBA, and in Fig. 4 for nitromethane. Detailed discussions of each run follow.

Table IV

RESULTS OF ADIABATIC SELF-HEATING EXPERIMENTS

Compound	Duration of Manual Control (hr)	Temp. at Beginning of Automatic Control (°C)	E_a (kcal M^{-1})	Temp. Range (°C)	$q\nu$ (cal g^{-1} sec^{-1})	Record No.
2, 2-DP	5	196	53.4	196-220	2.5×10^{22}	19-22
IBA	3	136	25.4	140-154	6.1×10^{11}	15-IBA
IBA	3	121				17-IBA
			112	121-123		
			10.4	123-150		
			33.9	150-168		
IBA	4	126	33.7	140-173	3.2×10^{15}	18-IBA
IBA	4	117	30.2	140-169	5.8×10^{14}	20-IBA
IBA	4	148	47.3	140-168	2.8×10^{22}	21-IBA
CH_3NO_2	4	207	28.0	250-340	6.5×10^{9}	22-NM
CH_3NO_2	4	231	45.9	231-300	4.2×10^{16}	23-NM
CH_3NO_2	4.5	238	44.2	238-292	1.1×10^{16}	24-NM

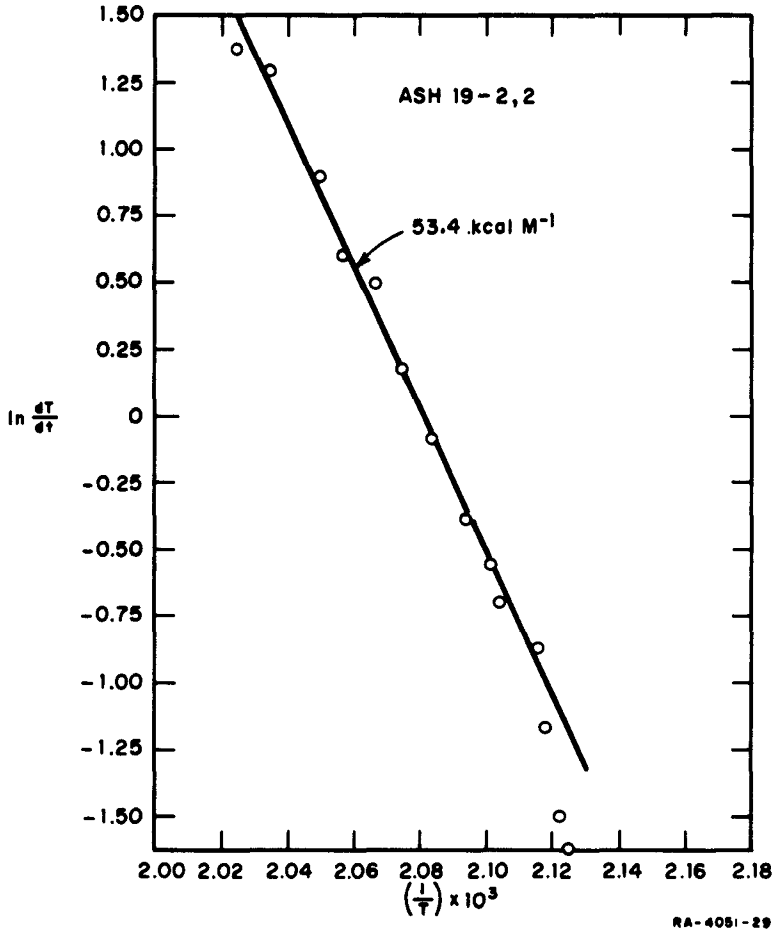

FIG. 2 PLOT OF ln dT/dt vs. 1/T FOR ADIABATIC SELF-HEATING EXPERIMENTS WITH 2,2 DP (U)

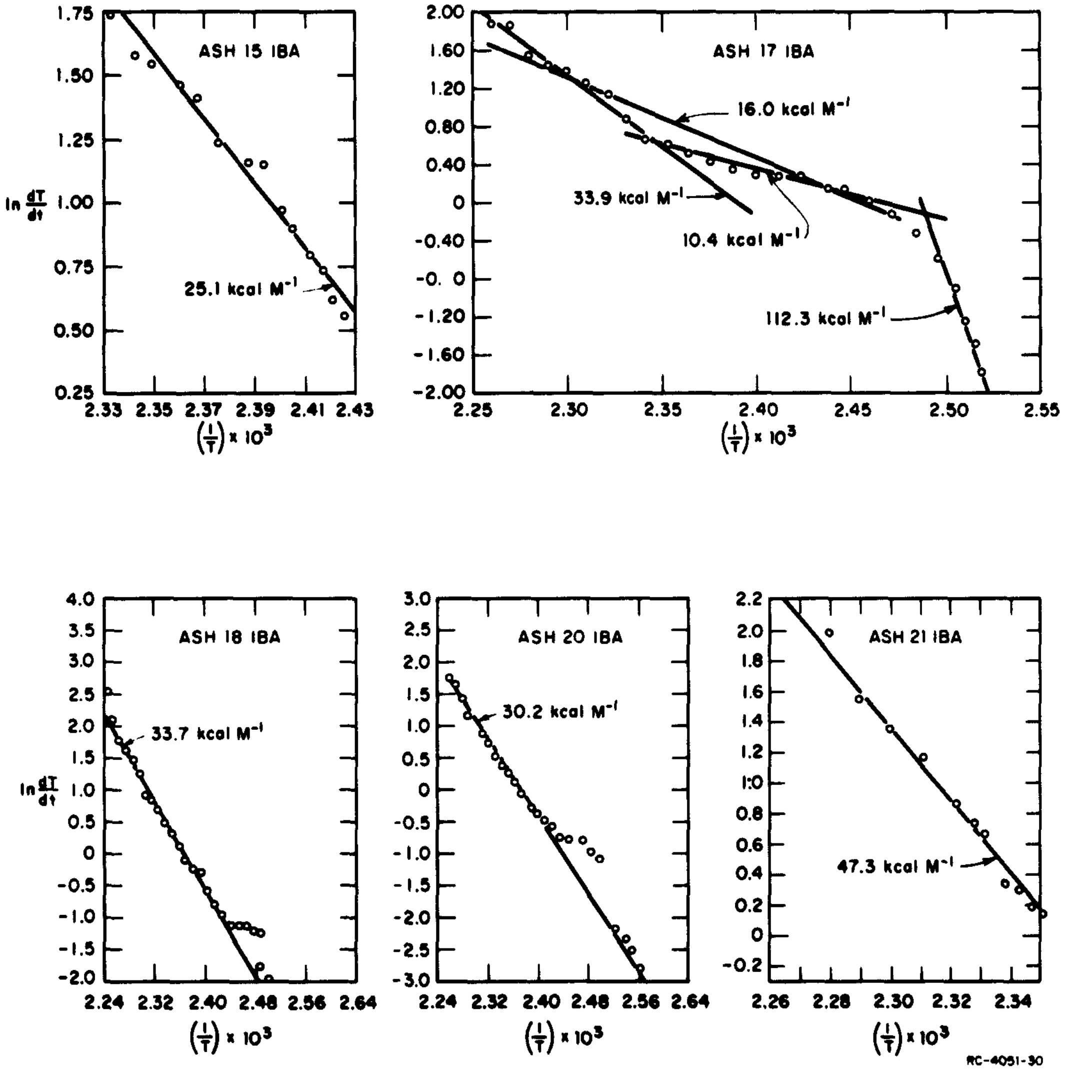

FIG. 3 PLOTS OF ln dT/dt vs. 1/T FOR ADIABATIC SELF-HEATING EXPERIMENT WITH IBA (U)

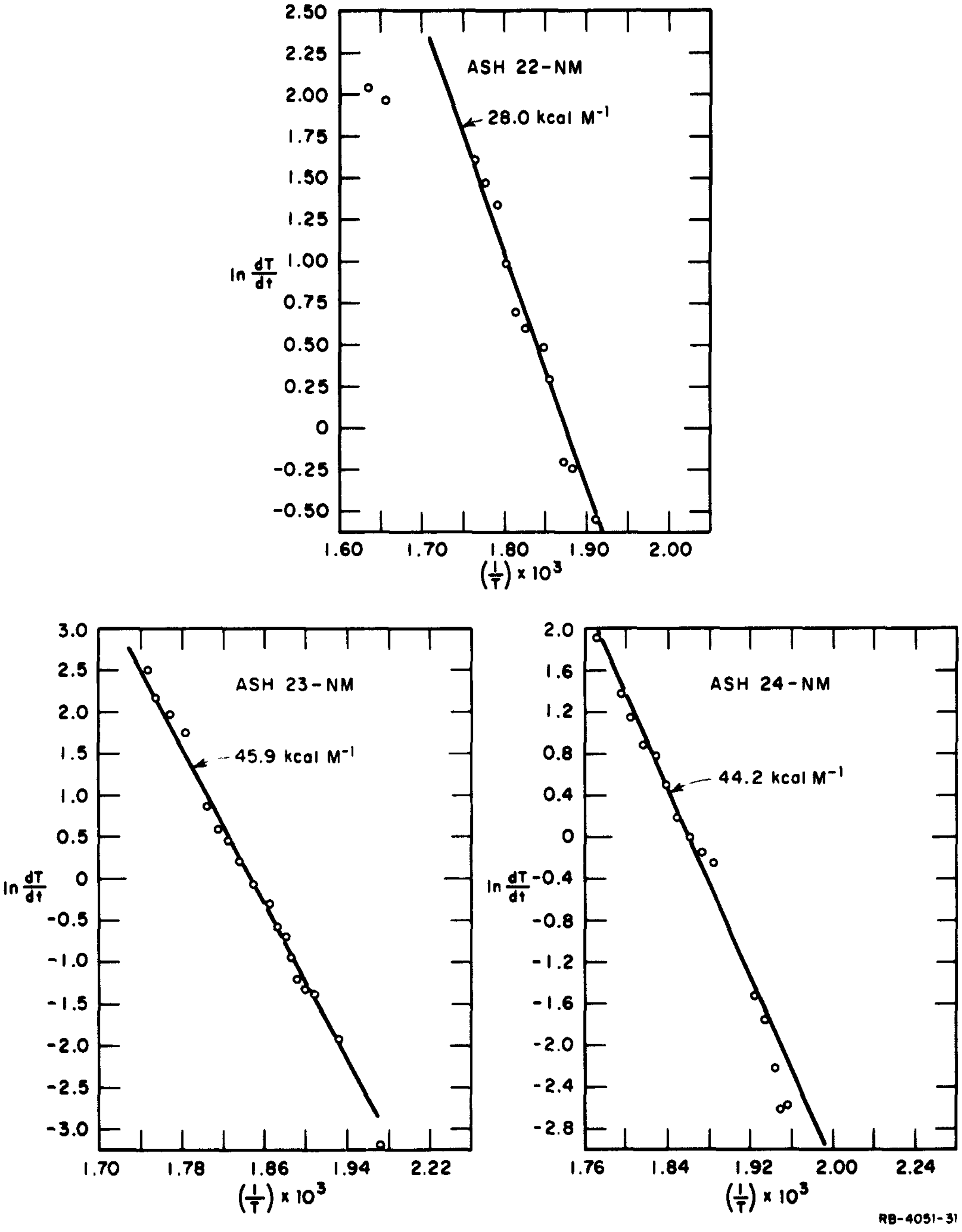

FIG. 4 PLOTS OF ln dT dt vs. 1/T FOR ADIABATIC SELF-HEATING EXPERIMENTS WITH NITROMETHANE (U)

1. 2, 2-DP

Run ASH 19-22 -- This experiment was initiated by heating the system for five hours until self-heating became detectable at 196°C. The remainder of the run and the data reduction were routine. Table V summarizes results from this and all previous runs on 2, 2-DP. Agreement is satisfactory.

Table V

2, 2-DP SELF-HEATING RESULTS

Run No.	E_a (kcal M^{-1})	$q\nu$ (cal g^{-1} sec^{-1})
ASH 11-22	47.2	---
ASH 12-22	54.0	6.3×10^{22}
ASH 14-22	51.7	2.9×10^{21}
ASH 19-22	53.4	2.5×10^{22}
Average	51.6 ± 2.2	$(3.0 \pm 2.2) \times 10^{22}$

2. IBA

Run ASH 15-IBA -- Self-heating was detected after a three-hour heating period, when the temperature of the system had reached 136°C. At this time the reaction was well under way and the experiment terminated in an explosion fifteen minutes after automatic control had been initiated. Data reduction presented no problem. However, the behavior of the sample during the initial stage of the reaction was not recorded. For this run $E_a = 25.4$ kcal M^{-1} and $q\nu = 6.1 \times 10^{11}$ cal g^{-1} sec^{-1}.

Run ASH 17-IBA -- The system was heated manually for three hours and checked for self-heating periodically after the temperature passed 85°. The first indication of self-heating was at 121°C, and automatic control was initiated at this temperature. Adiabatic control was good until the rate of temperature rise passed 4°C/minute (at 172°C). The data, when reduced, did not give a single straight line, but a curve with three distinct slopes. For the low temperature section of the curve (121 to 123°C), E_a = 112 kcal M^{-1}, for the mid-temperature range (123-150), E_a = 10.4 kcal M^{-1}, and for the final temperature range (150-168°C), E_a = 33.9 kcal M^{-1}.

Run ASH 18-IBA -- After heating the system manually for four hours, self-heating was detected at 126°C. The system was placed on automatic control, and the temperature rose to 171°C before the experiment was terminated. Except for an initial uncertainty in the range, 126-140°C, the reduced data are representable as a straight line for which E_a = 33.7 kcal M^{-1} and $q\nu = 3.2 \times 10^{15}$ cal g^{-1} $sec.^{-1}$

ASH 20-IBA -- After the system was heated manually for four hours, self-heating was detected at 117°C. The system was placed on automatic control. The self-heating period continued for 2-1/2 hours before the heating became so rapid that control failed. As with ASH-18 IBA, there was anomaly between 126-140°C. Above this range, reduction of the data gave a straight line with E_a = 30.2 kcal M^{-1} and $q\nu = 5.8 \times 10^{14}$ cal g^{-1} $sec.^{-1}$

ASH 21-IBA -- Self-heating was noticed after four hours, at 148°C, significantly higher than for earlier runs. The data obtained reduced to a straight line with $E_a = 47.3 \times 10^3$ kcal M^{-1} and $q\nu = 2.8 \times 10^{22}$ cal g^{-1} $sec.^{-1}$ Since the IBA used in this run had been distilled two months previously, there may have been some change in the material. Unfortunately, no sample remained for chromatographic analysis and comparison with that of fresh material.

3. Nitromethane

ASH 22-NM -- The system was heated manually for four hours. Self-heating was observed at a temperature of 207°C and continued for about four hours. Adiabatic control was poor during most of the run, no better than ± 1°C. E_a for a range from 250 to 340°C was 28.0 kcal M^{-1}. $q\nu$ was calculated to be 6.5×10^9 cal g^{-1} $sec.^{-1}$

ASH 23-NM -- The system was heated manually for four hours. Self-heating was observed at a temperature of 231°C and continued for three hours to 300°C. Adiabatic control was excellent, ±0.15°C for most of the run. Reduction of the data gave a straight line with $E_a = 45.9$ kcal M^{-1}. $q\nu$ was calculated to be 4.2×10^{16} cal $g^{-1} sec^{-1}$.

ASH 24-NM -- The system was heated manually for 4.5 hours. Self-heating was observed at a temperature of 238°C. Adiabatic control was excellent for most of the run. E_a for a range from 238 to 292°C was 44.2 kcal M^{-1}. $q\nu$ was 1.1×10^{16} cal g^{-1} sec^{-1}.

The disagreement of data between run No. 22 on the one hand and runs 23 and 24 on the other may be a result of the extremely poor control experienced in run No. 22. The value of $E_a = 45$ kcal M^{-1}, and $q\nu = 2.5 \times 10^{-16}$ cal g^{-1} sec^{-1} obtained from runs 23 and 24 can be compared with previously reported values of 50.0 kcal M^{-1} by Hillenbrand and Kilpatrick,[9] and $E_a = 53.6$ kcal M^{-1}, $\nu = 10^{14.6}$ sec^{-1} by Cottrell, Graham, and Reid.[10]

B. Future Plans

No further work is planned with 2,2-DP in Type II bombs, but at least one more run will be made with IBA and two with nitromethane. The thinner-walled vessels (Type III) will be used for runs with 2,2-DP to test the assumptions (see reference 1) used in calculating $q\nu$. These Type III vessels should be available by the middle of October.

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[9] L. J. Hillenbrand and M. L Kilpatrick, J. Chem. Phys. 1953, 21 (525)

[10] T. L. Cottrell, T. E. Graham, and T. Y. Reid, Trans. Far. Soc. 47, 584 (1951)

IV KINETICS OF THERMAL DECOMPOSITION

(Theodore Mill)

A. Mechanism and Kinetics of Thermal Decomposition of 1,2-DP

1. Decomposition of Neat 1,2-DP

Kinetics of the decomposition of the pure liquid was measured at 155° C in sealed capillary tubes containing 70-90 mg of purified 1,2-DP. The first experiments resulted in nonviolent rupture of the tubes with indication of extensive decomposition of the material. This effect was thought to be due to self-heating of the 1,2-DP induced by its high concentration and the poor thermal conductivity of the thick glass walls. Several tubes were prepared with thin platinum wires extending the length of the interior. These tubes did not rupture under conditions in which control tubes without wires did.

Results of these experiments indicate that 1,2-DP has a half-life of about twenty hours at 155° C. This number could be low by about 20 per cent or high by 10 per cent. One may calculate a value of the half-life from the kinetic rate law which describes solution kinetics at 176-187° C (see reference 1, p. 56) using extrapolated values for k_1 and k_2. The initial concentration of 1,2-DP was inserted into the equation and values of 1,2-DP concentration at intervals of time were computed. The half-life calculated in this way was 5.4 hours. Agreement between the experimental and calculated values is within experimental error despite their four-fold difference (an uncertainty of 2 kcal/mole in E_a gives an uncertainty of a factor of ten in the rate of this temperature). The rate equations thus appear to be applicable to the decomposition of the pure liquid.

A subsequent measurement of k_1 at 155° C in nitrobenzene solution gave a value one-fifth of that obtained by extrapolation from 187° C. This may account for the disagreement between calculated and measured half-lives in pure liquid.

2. Solvent Effects

The above data suggest that a change in solvent from nitrobenzene to 1,2-DP has little effect on the rate of decomposition of 1,2-DP. The rates of decomposition of 1,2-DP in chloronapthalene and hexadecane have been measured. Table VI summarizes the data. All rates at one temperature are identical within experimental error, indicating an absence of a kinetic solvent effect, despite a significant variation in solvent dielectric.

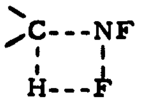
Table VI

SOLVENT EFFECTS IN 1,2-DP DECOMPOSITION

Solvent	1,2-DP (moles/liter)	Temp. (° C.)	$k_1 \times 10^2$ (a) (hr^{-1})	$t_{1/2}$ (min)
Nitrobenzene	0.490	187	10.8	200
	0.461	176	3.5	519
Chloronapthalene	0.649	187	8.9	200
Hexadecane	0.462	187	9.7	260
	0.406	176	3.5	485

(a) Least-squares values

We have suggested (see reference 1, pp. 46-49) that the rate-controlling step in decomposition of 1,2-DP must involve loss of HF. The absence of solvent effect indicates that there is little charge separation in the transition state; this implies a concerted, four-center type of mechanism:



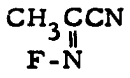
3. Structure of Intermediate [(N-fluoroimino) propionitrile]

The previous quarterly report described analytical data on the intermediate product isolated from the decomposition of 1,2-DP. The data led to the tentative identification of the product as 2-(N-fluoroimino) propionitrile. Elemental analyses and NMR spectra provide additional evidence for this structural assignment, viz:

Anal. for $C_3H_3N_2F$

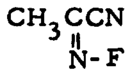
	C	H	N	F
Calculated:	41.95	3.49	32.6	22.1
Found:	43.49	4.34	31.24	21.56

These results confirm the empirical formula indicated. The NMR spectra were prepared on a sample purified by gas chromatography and dissolved in CCl_4 (10% by wt.). The spectra were surprising and deserve some discussion. The H^1 NMR spectrum consists of a singlet at 7.66τ and a doublet at 7.74τ, $J \sim 1$ cps (equal band areas). The F^{19} NMR spectrum has a multiplet at -66.7 ppm, $J \sim 1$ cps and a singlet at -53.2 ppm from CCl_3F. Clearly the splittings are due to a weak H-F coupling. The low-field position of the fluorine resonance bands seems to rule out C-F structures and confirms an N-F structure. Since there are two kinds of protons and fluorines in the compound having only one fluorine atom per molecule, we conclude that the compound is a mixture of the syn and anti isomers of 2-(N-fluoroimino) propionitrile.



$CH_3\underset{\text{F-N}}{\overset{\|}{C}}CN$

syn



$CH_3\underset{\text{N-F}}{\overset{\|}{C}}CN$

anti

A weak through-space coupling of the protons and fluorine in the syn isomer accounts for the observed splitting and small coupling constant. A recent study of syn-anti oxime isomer NMR spectra indicates that the relative position of the α-methylene protons is a function of both structure and solvent, but syn-methylene protons are often found upfield from the anti-protons.[11]

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[11] G. Karabatsos, R. A. Taller, and F. M. Vane, J. Amer. Chem. Soc., 85, 2327 (1963)

B. Mechanism and Kinetics of Thermal Decomposition of 2, 2-DP

1. Kinetic Rate Law

A series of experiments with nitrobenzene solutions of 2, 2-DP over a 60-fold change in 2, 2-DP concentration indicated no change in the initial rate constant, evaluated from a log concentration vs. time plot (Table VII). The reaction becomes autocatalytic at later stages.

Table VII

DECOMPOSITION OF 2, 2-DP IN
NITROBENZENE AT 190°C

2, 2-DP (moles/liter)	$k_1 \times 10^2$ [a] $(hr)^{-1}$
0.414	0.015
0.145	$\sim$ 0.008
0.061	0.018
0.0066	0.017

(a) Least-squares values

These rate data were used to calculate values of the autocatalysis rate constant and exponent in the equation of the form used for 1, 2-DP:

$$\text{rate} = k_1 (A - x) + k_2 (A - x) (x)^n \qquad (4)$$

where A is the original concentration of 2, 2-DP and x is the amount decomposed. Only a poor correlation was found for the rate data with this equation: $k_2 \sim 200k_1$, $n \sim 1.5$. These values compare with $k_2 = 64k_1$ and $n = 2$ at 187° for 1, 2-DP. (See reference 1, p. 46.)

2. Solvent Effect

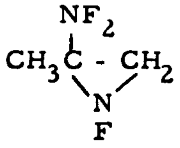
One run was made in hexadecane at 190°, with a 0.476 molar solution of 2, 2-DP. The first-order rate constant was unchanged from nitrobenzene.

3. Reaction of 2,2-DP with Base

The facile reaction of 1,2-DP with butoxide ion is due to ease of loss of HF (see reference 1, p. 42) and is similar mechanistically to the thermal decomposition. There is no obviously easy way for 2,2-DP to lose HF and one expects it to react very slowly with butoxide unless direct substitution of N-fluorine is rapid. Some 2,2-DP was distilled into n-butanol to give ∿0.1 molar solution. Sodium butoxide (1 M) in butanol was added. The 2,2-DP concentration was unchanged after 24 hours. Thus, direct attack on N-fluorine by butoxide ion is negligible under conditions where HF elimination in the 1,2 isomer is very rapid.

A brief survey of the literature indicates that primary or secondary NF compounds are very susceptible to base-promoted HF elimination but tertiary NF compounds are relatively stable to attack by a variety of basic reagents.[12] When reaction does occur, the products are those derived from attack on the N-F rather than C-N bonds.

The substantially slower rate of thermal decomposition of 2,2-DP compared with 1,2-DP and the apparent initial first-order character of the reaction are consistent with a mechanism involving loss of HF to give an N-fluoropropyleneimine structure.



C. Future Work

Experiments will be made to isolate and identify the intermediate products from the decomposition of 2,2-DP. A study of the polymeric residue from this reaction will be made to establish its structural features and role in autocatalysis.

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[12] K. Baum, Aerojet-General Corporation, First Propellant Contractor's Synthesis Conference, New York, April 1963, p. 328 et. seq.

Kinetics of decomposition of other isomers and homologs of 1, 2-DP will be measured as soon as the compounds become available.

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