AD-783 960

THE THERMAL DECOMPOSITION OF THIRTY COMMERCIALLY AVAILABLE MATERIALS AT 300C

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Prepared for:

Department of Transportation

February 1974

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: NOLTR 74-44
2. GOVT ACCESSION NO.:
3. RECIPIENT'S CATALOG NUMBER: AD-783 960
4. TITLE (and Subtitle): THE THERMAL DECOMPOSITION OF THIRTY COMMERCIALLY AVAILABLE MATERIALS AT 300 DEGREES C
5. TYPE OF REPORT & PERIOD COVERED: Final Report
6. PERFORMING ORG. REPORT NUMBER:
7. AUTHOR(s): Eleonore G. Kayser
8. CONTRACT OR GRANT NUMBER(s): DOT-AS-30044
9. PERFORMING ORGANIZATION NAME AND ADDRESS:

Chemistry Research Department
Naval Ordnance Laboratory
White Oak, Silver Spring, Maryland 20910

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:

DOT-AS-30044
NOL 798/DOTX0123

11. CONTROLLING OFFICE NAME AND ADDRESS:
12. REPORT DATE: February 1974
13. NUMBER OF PAGES: 35
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office):
15. SECURITY CLASS. (of this report): UNCLASSIFIED
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:
16. DISTRIBUTION STATEMENT (of this Report): Approved for public release; distribution unlimited.
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report): This research was monitored by the Department of Transportation.
18. SUPPLEMENTARY NOTES:
19. KEY WORDS (Continue on reverse side if necessary and identify by block number):

Thermally Unstable Materials
Hazardous Materials
Transportation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A literature search of available thermochemical data of twenty-six organic and inorganic compounds tabulated in the Department of Transportation's commodity listing has been completed. Experiments have been carried out to measure the thermal sensitivity of these materials in laboratory tests using thermal surge stimuli, differential scanning calorimetry, and a system designed to determine qualitatively the percent decomposition of liquid and solid materials at the limiting parameters designated by DOT (one hour at 300 degrees C). The amount
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20. Abstract (Cont)

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Under Interagency Agreement DOT-AS-30044, the Naval Ordnance Laboratory has completed a literature search of available thermochemical data of twenty-six organic and inorganic compounds tabulated in the Department of Transportation's commodity listing. Experiments have been carried out to measure the thermal sensitivity of these materials in laboratory tests using thermal surge stimuli, differential scanning calorimetry, and a system designed to determine quantitatively the percent decomposition of liquid and solid materials at the limiting parameters designated by DOT (one hour at 300°C). The amount of gas resulting from this thermal decomposition is also reported for the thirty-two compounds tested. This is the final report under that agreement. Use of trade names herein does not constitute any endorsement of the products named.

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By direction

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INTRODUCTION

The Department of Transportation (DOT) is considering the adoption of regulations that would furnish a more complete identification of the stability characteristics and therefore the potential hazards associated with the transport of hazardous materials. The Hazard Information (HI) system which is DOT's proposed means for upgrading hazardous materials (HM) labels and placards, is designed to inform individuals of the factual hazards of materials in transport and also to provide the necessary emergency response direction for those persons who are faced with an HM incident. Since these regulations would cover thermally unstable materials, an investigation was undertaken to characterize the behavior of several commercially available materials which could be so designated. A thermally unstable material is defined by DOT as "a commodity offered for transportation which is capable of undergoing an exothermic reaction without the addition of air or other chemical substances at a temperature less than 500°C".

The materials tested were selected from DOT's Commodity List of Hazardous Materials[1]. An important consideration for DOT is the conditions of which materials might be subjected during transport. The limiting parameters (maximum temperature and time) representing an extreme under normal shipping conditions were designated by DOT as one hour at 300°C.

An experimental evaluation of the thermal stability of these materials was performed, as well as a literature search of available thermochemical data and decomposition temperatures and incident reports resulting from accidents (fires and/or explosions). The experimental evaluation consisted of (a) thermal surge measurements of all liquids and liquefiable solids with melting points <200°C, and (b) differential scanning calorimetry measurements of all solids. A thermal stability test which could accommodate liquid and solid samples and which was used to determine both the total gas pressure evolved in the sample's decomposition and the percent material decomposition was also developed in this work.

EXPERIMENTAL

Tests of sensitivity to thermal surge were performed using the apparatus previously developed at NOL [2,3,4]. In this thermal initiation measurement, a 2.1μl sample is enclosed in a 6.35 cm length of stainless steel tubing which is then pulse-heated to temperatures in the range of 300-1000°C by a capacitor discharge. Both the temperature of the sample container and the time delays to explosion which fall in the range of 50-1000μsec were determined by measuring the resistance of the tubing as a function of time. Data plots of the logarithm of delay time to explosion as a function of the reciprocal of the absolute temperature (Figure 1) and the 250μsec delay time to explosion were obtained for liquids and liquefiable solids (Table 1).

Thermal decomposition studies with the Perkin Elmer Differential Scanning Calorimeter (DSC-1B)[5,6,7,8] could be determined only on solid materials due to the temperature and time parameters specified by DOT. Milligram quantities of material were used in each test. Depending on the melting point and/or the degree of sublimation, either the crimped cup or the hermetically sealed cup which withstands an internal pressure of ~28 psi were used. Since accurate temperaure information is desired, the calorimeter was calibrated at well known transition points of pure materials over the temperature range of 45°-300°C (Figure 2) at conditions identical to those of the projected analyses. The temperature of the samples was increased at a programmed rate of 10°/minute from 45°-300°C and then run isothermally at 300°C for one hour since a knowledge of the chemical behavior of materials at various temperatures is also important in judging chemical stability. The DSC thermograms provided information on possible decomposition as well as phase transitions taking place within the samples. The temperatures of all endotherms and exotherms were noted, as was the initial and final weight of material (Table 2).

Insofar as neither of the preceding tests were applicable to both liquid and solid materials, an investigation was undertaken to develop the preliminary design for such a test. A system was developed which was equipped to measure the percent material decomposition as well as total gas evolution (Tables 3,4); it was designed to handle all materials except gases. The materials were weighed on an Ainsworth balance (type SCV), sealed in melting point capillary tubes (1.6-1.8 x 90 mm, total free volume 114μl) at room temperature and placed in a 300°C heating block for a total time of 75 minutes. The capillary tubes were then cooled to room temperature, added to a sample tube (see Figure 3) containing 0.8 ml inert solvent (e.g., $(CH_3)_2CO$, CCl_4, $CHCl_3$, $(CH_3)_2SO$), broken and mixed. The % decomposition was then quantitatively determined by either (a) thin layer chromatography (TLC), (b) ultraviolet spectroscopy (UV), (c) gas chromatography (GC) or (d) NMR analysis of the residual material. The nuclear magnetic resonance (NMR) analyses required the use of deuterated solvents.

Utilizing a peak normalization technique coupled with the addition of an internal standard (e.g., dimethyl sulfoxide, 2,3-dimethyl-2,3-dinitrobutane, or toluene) an accurate assay (± 5%) of all test materials containing protons was obtained with the Varian HA-100 nuclear magnetic resonance spectrometer.

The percentage decomposition of materials not containing protons but displaying some degree of thermal instability such as weight loss or gas evolution, was quantitatively determined on either (a) F&M Scientific 5750 Research Chromatograph (thermal conductivity detector) or (b) Cary 14 Recording Spectrophotometer.

The apparatus selected for the gas evolution measurement consisted of a U-type manometer (Arthur H. Thomas Catalog No. 2984-D 25) with a rubber reservoir. The reservoir is connected at the bottom of the U-bend and is used for adjusting the mercury level in the manometer by means of a screw-type pinch clamp (Figure 3). One arm of the manometer is open to the atmosphere; the other arm terminates in a 3-way stopcock which permits venting and gassing the reaction vessel. The latter arm is connected by a T-joint, just below the stopcock, to a sample tube. The sample tube used was a modified Pyrex test tube with a central stopcock and a ground glass joint to match the side arm fitting from the manometer. Dow Corning vacuum grease was used to insure a tight seal. When a pressure increase was shown by a drop in the level of the mercury in the manometer arm attached to the sample tube, the screw clamp was used to force the mercury in that arm back to its original level thereby maintaining constant volume. After heating, the capillary tubes were cooled to room temperature and placed inside the sample tube (free volume 3.4 cc) which was then attached to the manometer (free volume 1.9 cc). The fiducial mark on the manometer was recorded, the stopcock was closed to seal the system and the capillary broken. Any pressure increase (shown by a drop in the level of the mercury in the manometer arm) was then recorded.

A heating block [9,10,11] consisting of a cylindrical aluminum core (8" O.D., 12" long) was used to maintain sample temperature at 300°C ± 0.2°C during the test. Since the test parameters of one hour at 300°C were specified by DOT, an iron-constantan thermocouple was placed in a capillary tube and heated under identical conditions as the projected analyses to determine the amount of time necessary for the samples to reach 300°C (Figure 4). An additional time period of 15 minutes in the heating block was added to the sample time to compensate for this.

TEST RESULTS

The materials selected for thermal stability testing along with their respective formulas and present hazard classifications are listed in Table 5.

The results of the the literature survey consisting of available (a) thermochemical data (heats of formation, combustion, explosion, decomposition, and polymerization), (b) decomposition temperatures, and (c) references to incidents (fires and explosions), can be found in Table 6. Of the thirty organic and inorganic materials listed, styrene monomer, acrylonitrile, 95% hydrazine, and 85% hydrazine hydrate were found to have a positive heat of formation. Six of the inorganic materials, namely, 30% hydrogen peroxide (H_2O_2), ammonium nitrate (NH_4NO_3), sodium azide (NaN_3), sodium permanganate ($NaMnO_4 \cdot 3H_2O$), potassium persulfate ($K_2S_2O_8$), and potassium permanganate ($KMnO_4$) were identified as having decomposition temperature below 300°C. However, our experimental evidence shows that sodium azide does not decompose below 300°C.

As can be seen in Tables 2, 3, and 4, the preceding materials, with the exception of sodium azide, were the only inorganic compounds found to decompose at the test conditions of one hour at 300°C. Neither endotherms nor exotherms occurred in the barium peroxide, potassium perchlorate, and sodium azide thermograms (Table 2). Endotherms noted in the sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) and barium perchlorate ($Ba(ClO_4)_2 \cdot 3H_2O$) thermograms were due to the loss of water from the crystal, while those observed in the sodium nitrite, sodium nitrate, potassium nitrate, and ammonium perchlorate thermograms correspond to phase transitions within the solids. With the exception of m-dinitrobenzene and sym-trinitrobenzene, all the solid organic materials tested on the DSC displayed some degree of decomposition below 300°C (Table 2).

The percentage decomposition data for thirty-five organic and inorganic materials utilizing the sealed tube procedure can be found in Table 3. The following compounds: trinitrobenzene, m-dinitrobenzene, ammonium perchlorate, potassium nitrate, sodium nitrite, sodium nitrate, sodium azide, barium nitrate, barium perchlorate, potassium perchlorate, and sodium dichromate were unaffected by the test conditions; the other materials showed evidence of decomposition. Of the fifteen organic compounds examined, eleven were found to decompose completely. Acetaldehyde, crotenaldehyde, and nitromethane showed only partial decomposition (80, 90, and 10% respectively).

The total pressure build-up resulting from material decomposition can be seen in Table 4. Styrene was found to polymerize completely under the test conditions; no evidence of gas evolution was found. The thermal decomposition of ammonium nitrate, m-dinitrophenol, ethyl nitrate, and chloropicrin resulted in a high production of gas which was found to be comparable to the total gas evolved in the decomposition of the reference materials trinitrotoluene (TNT) and trinitroanisole (TNA). Material reaction with ullage air was observed in the 95% hydrazine and possibly the guanidine nitrate samples (decrease in sample weight generating a corresponding increase in gas evolution).

The threshold initiation temperature in the thermal surge apparatus (lowest temperature at which initiation could occur) is reported in Tables 1 and 7. Only eleven organic materials of the thirty organic and inorganic materials could be tested on the thermal surge apparatus. Insofar as neither styrene nor acrolein could be initiated on the thermal surge apparatus, the maximum temperatures to which the samples could be raised is reported (Table 1). Data for 30% hydrogen peroxide could not be obtained due to material reaction with the stainless steel tubing, while that for acetaldehyde is not reported because of its low boiling point (21°C). The thermal surge data for inorganic materials such as: ammonium perchlorate, potassium nitrate, sodium nitrite, sodium azide, barium nitrate, potassium perchlorate, sodium dichromate, potassium persulfate, ammonium nitrate, sodium permanganate, potassium permanganate, sodium nitrate, barium peroxide, and barium perchlorate were also not reported due to either (a) melting point >200°C, or (b) material decomposition at or near the melting point. Of the materials tested, ethyl nitrate, chloropicrin, and nitromethane were found to have the lowest initiation temperatures (Table 1). Data plots of the logarithm of the delay time to explosion as a function of the reciprocal of the aboslute temperature are shown in Figure 1 for eleven organic and four reference materials.

CONCLUSIONS

Of the thirty organic and inorganic materials examined for thermal stability (one hour at 300°C as specified by DOT), only two organic materials (m-dinitrobenzene, trinitrobenzene) and ten inorganic materials (ammonium perchlorate, potassium nitrate sodium nitrite, sodium azide, barium nitrate, potassium perchlorate, sodium dichromate, barium peroxide, barium perchlorate, sodium nitrate) displayed no evidence of decomposition. All other materials, i.e., acetaldehyde, acrolein, acrylonitrile, ammonium nitrate, chloropicrin, crotonaldehyde, 30%-hydrogen peroxide, m-dinitrophenol ethyl nitrate, guanidine nitrate, 95% hydrazine, 85% hydrazine hydrate, 1,1-dimethylhydrazine, potassium persulfate, potassium permanganate, sodium permanganate, nitromethane, and styrene showed some degree of decomposition (Table 7). From the data submitted, acrolein, crotonaldehyde, 85% hydrazine hydrate, 1,1-dimethylhydrazine and styrene would not present as great a thermal hazard in transport as ammonium nitrate, chloropicrin, m-dinitrophenol, ethyl nitrate, nitromethane, 30% hydrogen peroxide, potassium permanganate and sodium permanganate.

As can be seen in Table 7, the hazard potential of these materials does not depend entirely on the percentage decomposition of material but also on (a) the amount of gas liberated in decomposition, (b) the flammability of the material and its products of decomposition, and (c) material reactivity with ullage air. Therefore, these factors should also be considered when calculating the degree of thermal hazard involved in the transport of any material.

Most organic materials (as can be seen from the preceding data) are unable to withstand the conditions for thermal stability as defined by DOT (one hour at 300°C). Whether these limits are practical or necessary, when considering the possible hazards associated with the transport of materials, must be determined by DOT.

Table 1

THERMAL SURGE DATA

#	Compound	Code	Threshold Initiation Temp. (°C)	250μsec Delay Time to Explosion (°C)
1.	Nitroglycerine*	NG	220°C	277°C
2.	Ethyl Nitrate		375	415
3.	Chloropicrin		325	637
4.	Trinitroanisole*	TNA	411	681
5.	Trinitrotoluene*	TNT	427	745
6.	2,4-Dinitrophenol	m-DNP	470	791 (extrapolated)
7.	Trinitrobenzene	TNB	460	848
8.	Nitrobenzene*	NB	530	>1000 (extrapolated)
9.	Acrylonitrile		710	810 (extrapolated)
10.	Crotonaldehyde		780	963 (extrapolated)
11.	Nitromethane	NM	370	682
12.	m-Dinitrobenzene	m-DNB	450	790
13.	1,1-Dimethylhydrazine		515	832
14.	95% Hydrazine		615	827
15.	85% Hydrazine Hydrate		625	920 (extrapolated)

Compound	Maximum Temperature (a) (°C)	Threshold Initiation Temp. (°C)
Styrene-monomer	818°C	----
Acrolein inhibited with Hydroquinone	748	----
Ethyl Acetate*	786	----
Benzene*	860	----
HOH*	823	----

(a) none of the above samples displayed an initiation temperature up to and including the maximum temperature to which the materials could be raised. This temperature is reported above.

* reference materials.

Table 2

DIFFERENTIAL SCANNING CALORIMETRY DATA

Material	Sample Wt. mgs	% Wt. Loss	Comments
AN (a)	3.0	92.3	Endotherms$_{pt}$ 80°, 128°. Endotherm$_{mp}$ 168°C.
AN (a)	5.0	100.0	Material boiling out of sample cup ≈ 220°. Large exotherm noted at ≈ 245°.
$Ba(ClO_4)_2 \cdot 3H_2O$	32.7	14.4	Weight loss due to loss of HOH from sample.
$Ba(ClO_4)_2 \cdot 3H_2O$	38.5	14.3	No exotherms noted.
$Ba(NO_3)_2$	45.8	0.0	Endotherm noted at 293°C. No exotherms noted.
$Ba(NO_3)_2$	34.0	0.0	
BaO_2	29.8	0.7	No endotherms nor exotherms noted.
BaO_2	35.5	0.0	
$KClO_4$	18.9	0.0	No endotherms nor exotherms noted.
$KClO_4$	28.4	0.0	
$KMnO_4$	31.8	12.6	Exotherm onset temp 271-273°C.
$KMnO_4$	27.5	12.4	
KNO_3	29.5	0.0	Endotherm$_{pt}$ 132°C. No exotherm noted.
KNO_3	33.0	0.0	
$K_2S_2O_8$ (a)	29.8	7.1	Exotherm temp. 256°C.
$K_2S_2O_8$ (a)	37.3	6.8	
NaCl*	24.1	0.0	No exotherm nor endotherms noted.
NaCl*	53.5	0.0	
$Na_2Cr_2O_7 \cdot 2H_2O$	21.6	11.6	Endotherms noted at 90° and 143°C.
$Na_2Cr_2O_7 \cdot 2H_2O$	17.4	11.6	No exotherm noted.
$NaMnO_4 \cdot 3H_2O$ (a)	33.0	27.6	Multiple endotherms noted from 200-221°C.
$NaMnO_4 \cdot 3H_2O$ (a)	30.0	40.1	Decomposition with melting.
NaN_3	7.8	0.0	No endotherms nor exotherms noted.
NaN_3	33.2	1.3	
$NaNO_2$	31.0	0.0	Endotherm$_{pt}$ 157°C. No exotherms noted.
$NaNO_2$	23.5	1.2	
$NaNO_3$	25.0	0.0	Endotherm$_{pt}$ 268°C. No exotherm noted.
$NaNO_3$	18.5	0.6	
NH_4ClO_4	5.9	0.0	Endotherm$_{pt}$ 232°C. Slight exotherm noted at ≈ 300°C.
NH_4ClO_4	21.3	0.3	
Gaunidine Nitrate	9.6	89.0	Melting with decomposition, onset temperature 204°C.
Gaunidine Nitrate	9.0	90.4	
m-Dinitrophenol (a)	9.0	84.3	Endotherm$_{mp}$ 100°C. Exotherm onset temperature 283°C.
m-Dinitrophenol (a)	4.0	93.7	
m-Dinitrobenzene (a)	7.0	0.0	Endotherm$_{mp}$ 88°c. No exotherm noted.
m-Dinitrobenzene (a)	3.0	0.0	
TNB (a)	3.0	0.0	Endotherm$_{mp}$ 123°C. No exotherms noted.
TNB (a)	5.0	0.0	
TNA* (a)	4.0	95.0	Endotherm$_{mp}$ 67°C. Exotherm onset temperature ≈ 248°C.
TNA* (a)	3.0	93.4	

Table 2 (Cont.)

DIFFERENTIAL SCANNING CALORIMETRY DATA

Material	Sample Wt. mgs	% Wt. Loss	Comments
TNT* (a)	3.0	93.0	Endotherm$_{mp}$ 82°C. Exotherm onset
TNT* (a)	2.0	94.5	temperature at 300°C.

Samples were run in a crimped cup unless otherwise noted.

All samples were programmed from 45°C - 300°C at 10°/minute and then run isothermally at 300°C for one hour.

* reference material

(a) Samples run in a sealed cup which withstands an internal pressure of ≈ 28 psi. The sealed sample cup was used for all material which tended to sublime during the temperature run.

Endotherm pt - phase transition mp - melting point
Temperatures reported are corrected temperatures.

Table 3

SEALED TUBE DECOMPOSITION DATA

Sample	Sample Weight mgs	Percent Weight Loss	Percent Decomposition	Test Procedure (a)	Comments
Acrolein	16.7	---	100.0	2	gas evolved, black material noticeable in tube.
Acrolein	16.4	---	100.0	2	
Acrolein	16.7	---	100.0	2	
Styrene-monomer	18.8	---	(b)	2	gas evolved, material polymerized.
Styrene-monomer	18.4	---	(b)	2	
Styrene-monomer	18.4	---	(b)	2	
KNO_3	66.5	0.0	0.0	1	no gas evolved, no evidence of decomposition.
KNO_3	32.2	0.0	0.0	1	
$NaNO_2$	53.0	0.4	---	1	no gas evolved, no evidence of decomposition.
$NaNO_2$	60.0	0.2	---	1	
$Ba(NO_3)_2$	89.2	0.4	---	1	no gas evolved, no evidence of decomposition.
$Ba(NO_3)_2$	65.7	0.5	---	1	
$KClO_4$	102.0	0.5	---	1	no gas evolved, no evidence of decomposition.
$KClO_4$	98.6	0.3	---	1	
NM	23.4	---	8.3	2	gas evolved, black material noticeable in tube.
NM	22.9	---	12.0	2	
NM	22.8	---	10.4	2	gas evolved, black material noticeable in tube.
NM	23.0	8.7	---	1	
$Na_2Cr_2O_7 \cdot 2H_2O$	63.6	0.0	0.0	1	no gas evolved, no evidence of decomposition.
$Na_2Cr_2O_7 \cdot 2H_2O$	33.5	1.0	---	1	
NaN_3	32.1	0.0	0.0	1	no gas evolved, no evidence of decomposition.
NaN_3	24.2	0.0	0.0	1	
HOH*	84.3	0.0	0.0	1	no gas evolved, no evidence of decomposition.
HOH*	20.5	0.0	0.0	1	
HOH*	27.3	---	0.2	2	
30% H_2O_2	23.4	---	---	-	ec after ≈25 min in heating block.
30% H_2O_2	22.7	---	---	-	ec in heating block.
30% H_2O_2	7.3	---	100.0	2	gas evolved.
30% H_2O_2	5.0	---	100.0	3	gas evolved.
Crotonaldehyde	17.5	---	88.9	2	gas evolved, rust colored solution in tube.
Crotonaldehyde	17.9	---	87.7	2	
Crotonaldehyde	17.8	---	88.6	2	
Ethyl acetate*	27.6		0.0	2	no gas evolved, no evidence of decomposition.
Ethyl acetate*	18.3		0.0	2	
$NaNO_3$	60.0	0.0	0.0	1	no gas evolved, no decomposition.
$NaNO_3$	63.2	0.0	0.0	1	no gas evolved, no decomposition.

Table 3 (Cont.)

SEALED TUBE DECOMPSOITION DATA

Sample	Sample Weight mgs	Percent Weight Loss	Percent Decomposition	Test Procedure (a)	Comments
Acrylonitrile	16.6	1.5	100.0	2	black charred material in tube, no noticeable gas accumulation.
Acrylonitrile	16.1	0.0	100.0	2	
m-Dinitrobenzene	24.1	0.0	0.0	2	no evidence of decomposition.
m-Dinitrobenzene	30.3	0.0	0.0	2	
m-Dinitrophenol	13.8	---	100.0	2	gas evolved, black charred material in tube.
m-Dinitrophenol	18.7	---	100.0	2	
Guanidine nitrate	12.2	---	100.0	2	gas evolved in decomposition
Guanidine nitrate	20.2	---	100.0	2	
95% Hydrazine	30.0	---	---	-	ec in heating block.
95% Hydrazine	15.2	---	---	-	ec in heating block.
95% Hydrazine	10.0	---	---	-	ec in heating block.
95% Hydrazine	7.1	---	100.0	2	gas evolved.
95% Hydrazine	4.0	---	100.0	2	gas evolved.
85% Hydrazine hydrate	16.2	---	100.0	2	gas evolved.
	10.2	---	100.0	2	gas evolved.
1,1 Dimethyl-hydrazine	10.1	---	100.0	2	gas evolved.
	7.1	---	100.0	2	gas evolved.
Ethyl nitrate	3.0	---	---	-	ec in heating block.
Ethyl nitrate	1.3	---	100.0	2	gas evolved.
Ethyl Nitrate	0.9	---	100.0	2	gas evolved.
$NaMnO_4 \cdot 3H_2O$	21.2	---	---	-	ec in heating block.
$NaMnO_4 \cdot 3H_2O$	13.4	---	---	-	ec in heating block.
$NaMnO_4 \cdot 3H_2O$	3.0	---	100.0	3	gas evolved in decomposition.
$NaMnO_4 \cdot 3H_2O$	2.2	---	100.0	3	
$KMnO_4$	17.0	---	---	-	ec in heating block.
$KMnO_4$	11.3	---	---	-	ec in heating block.
$KMnO_4$	5.5	---	---	-	ec in heating block.
$KMnO_4$	3.0	---	98.0	3	gas evolved in decomposition.
$KmnO_4$	2.0	---	100.0	3	
Acetaldehyde	17.3	---	80.0	2	gas evolved, brown colored solution in tube, ≈ 15% crotonaldehyde formed in the decomposition.
Acetaldehyde	17.0	---	82.0	2	
$Ba(ClO_4)_2 \cdot 3H_2O$	79.3	0.0	0.0	1	no gas evolved, no decomposition.
$Ba(ClO_4)_2 \cdot 3H_2O$	64.1	0.0	0.0	1	
NaCl*	55.2	0.3	0.0	1	no gas evolved, no evidence of decomposition.
NaCl*	65.0	0.0	0.0	1	
TNB	11.6	0.9	---	1	no gas evolved, no evidence of decomposition.
TNB	19.3	0.5	---	1	
TNB	22.0	---	0.0	2	
TNB	18.6	---	0.7	2	no gas evolved, no evidence of decomposition.
TNB	15.7	---	0.6	2	
TNB	12.8	---	0.4	2	

Table 3 (Cont.)

SEALED TUBE DECOMPOSITION DATA

Sample	Sample Weight mgs	Percent Weight Loss	Percent Decomposition	Test Procedure (a)	Comments
TNT*	19.8	---	---	-	ec after ≈ 5 min in heating block.
TNT*	11.3	---	---	-	ec in heating block.
TNT*	3.5	---	100.0	2	gas evolved, charred material left in sample tube.
TNT*	3.0	---	100.0	2	
TNT*	3.0	---	100.0	5	
$K_2S_2O_8$	39.7	5.8	---	1	gas evolved.
$K_2S_2O_8$	29.9	5.4	---	1	gas evolved.
NH_4ClO_4	27.3	0.0	0.0	1	no gas evolved, no evidence of decomposition.
NH_4ClO_4	33.8	0.0	0.0	1	
NH_4NO_3	32.4	---	---	-	ec after ≈20 min in heating block.
NH_4NO_3	41.1	---	---	-	ec in heating block.
NH_4NO_3	10.1	52.5	---	1	liquid left in tube.
NH_4NO_3	5.2	---	100.0	2	gas evolved, liquid in tube.
NH_4NO_3	7.3	---	100.0	5	
NB*	30.6	---	0.0	2	no gas evolved, no evidence of decomposition.
NB*	24.2	---	0.0	2	
NB*	24.6	0.0	0.0	1	
TNA*	23.6	---	---	-	ec in heating block
TNA*	21.8	---	---	-	ec in heating block
TNA*	5.0	---	100.0	2	gas evolved, charred material left in tube.
TNA*	3.5	---	100.0	2	
TNA*	3.5	---	100.0	5	
Chloropicrin	31.4	---	100.0	4	gas evolve, dark brown liquid in tube.
Chloropicrin	31.3	---	100.0	4	

(a) Test procedures used in determining % decomposition:

1. Weight loss.
2. NMR spectroscopy using an internal standard.
3. UV and colorimetric spectroscopy.
4. Gas chromatography.
5. Thin layer chromatography.

(b) 100% polymerized

* reference material

Table 4

GAS EVOLUTION DATA

Material	Sample Wt. mgs	Gas Evolved mm of Hg/ mg of material
$KMnO_4$	8.0	14.2
$KMnO_4$	8.0	12.7
$NaMnO_4 \cdot 3H_2O$	6.1	14.7
$NaMnO_4 \cdot 3H_2O$	3.7	14.3
$K_2S_2O_8$	11.0	6.3
$K_2S_2O_8$	11.6	6.1
TNT*	2.3	46.4
TNT*	3.5	48.6
AN	3.4	41.5
AN	3.9	40.8
TNA*	4.0	52.7
TNA*	3.3	55.1
NM	23.3	4.9
NM	22.8	4.4
Crotonaldehyde	17.4	7.6
Crotonaldehyde	17.6	7.4
Styrene-monomer	18.5	0.0
Styrene-monomer	18.6	0.0
85% Hydrazine	21.0	7.3
85% Hydrazine	20.9	7.5
95% Hydrazine	11.6	10.2
95% Hydrazine	6.7	32.1
95% Hydrazine	7.7	ec
1,1-Dimethyl hydrazine	6.0	6.5
1,1-Dimethyl hydrazine	5.9	6.6
Acrylonitrile	16.4	1.7
Acrylonitrile	16.7	1.7
NB*	25.1	-0.2 (a)
NB*	24.8	-0.2 (a)
Acrolein + HQ	5.2	9.2
Acrolein + HQ	10.1	9.3
HOH*	42.3	0.0
HOH*	42.5	0.0
Ethyl nitrate	2.7	39.6
Ethyl Nitrate	1.7	34.1
Acetaldehyde	14.4	9.2
Acetaldehyde	16.6	10.1
H_2O_2 - 30%	7.5	15.2
H_2O_2 - 30%	6.4	14.5
Chloropicrin	35.5	ec (b)
Chloropicrin	10.6	ec (b)
Chloropicrin	7.5	ec (b)

Table 4 (Cont.)

GAS EVOLUTION DATA

Material	Sample Wt. mgs	Gas Evolved mm of Hg/ mg of material
m-DNB	17.8	0.0
m-DNB	24.1	0.0
m-DNP	2.9	41.0
m-DNP	1.0	41.0
Guanidine nitrate	12.1	10.1
Guanidine nitrate	19.1	7.1
TNB	15.7	0.0
TNB	22.0	0.0

---

ec = exceed capacity of manometer

(a) negative pressure possibly due to presence of nitroso in the sample.

(b) gas produced by chloropicrin decomposition reacts with the mercury in the manometer.

* reference material

Total free volume of the capillary tube = 114μl.
Gas measurements were made on a constant volume system.
Total free volume of the entire system = 5.2 ± 0.1 cc.

Table 5

MATERIAL TESTED FOR THERMAL STABILITY

Material	Formula	DOT Hazard Classification
Acetaldehyde	CH_3CHO	flammable liquid
Acrolein	CH_2CHCHO + hydroquinone as inhibitor	flammable liquid
Acrylonitrile	CH_2CHCN	flammable liquid
Ammonium Nitrate	NH_4NO_3	oxidizing material
Ammonium Perchlorate	NH_4ClO_4	oxidizing material
Barium Nitrate	$Ba(NO_3)_2$	oxidizing material
Barium Perchlorate	$Ba(ClO_4)_2 \cdot 3H_2O$	oxidizing material
Barium Peroxide	BaO_2	oxidizing material
Benzene*	C_6H_6	flammable liquid
Chloropicrin	CCl_3NO_2	poisonous liquid class B
Crotonaldehyde	$CH_3CHCHCHO$	flammable liquid
1,1-Dimethylhydrazine	$(CH_3)_2NNH_2$	flammable liquid
Ethyl Acetate*	CH3COOC2H5	flammable liquid
Ethyl Nitrate	$C_2H_5ONO_2$	flammable liquid
Guanidine Nitrate	$NH_2CNHNH_2 \cdot HNO_3$	oxidizing material
95% Hydrazine	NH_2NH_2	corrosive liquid
85% Hydrazine	$N_2H_4 \cdot N_2O$	corrosive liquid
30% Hydrogen Peroxide	H_2O_2	corrosive liquid
m-Dinitrobenzene	$C_6H_4(NO_2)_2$	poisonous solid class B
m-Dinitrophenol	$(NO_2)_2C_6H_3OH$	solins. classified as poison B
Nitrobenzene*	C6H5NO2	poison liquid class B
Nitromethane	CH_3NO_2	-------
Potassium Nitrate	KNO_3	oxidizing material
Potassium Perchlorate	$KClO_4$	oxidizing material
Potassium Permanganate	$KMnO_4$	oxidizing material
Potassium Persulfate	$K_2S_2O_8$	-------
Sodium Azide	NaN_3	poisonous solid class B

Table 5 (Cont.)

MATERIALS TESTED FOR THERMAL STABILITY

Material	Formula	DOT Hazard Classification
Sodium Chloride*	$NaCl$	-------
Sodium Dichromate	$Na_2Cr_2O_7 \cdot 2H_2O$	oxidizing material
Sodium Nitrate	$NaNO_3$	oxidizing material
Sodium Nitrite	$NaNO_2$	oxidizing material
Sodium Permanganate	$NaMnO_4 \cdot 3H_2O$	oxidizing material
Styrene-Monomer	$C_6H_5CHCH_2$	-------
Trinitroanisole*	$(NO_2)_3C_6H_2OCH_3$	high explosive
Trinitrobenzene	$C_6H_3(NO_2)_3$	high explosive
Trinitrotoluene*	$(NO_2)_3C_6H_2CH_3$	high explosive
Water*	HOH	-------

* reference materials

Table 6

THERMOCHEMICAL DATA

Material	Decomposition Temp. °C	Reference	Heat of Formation	Reference
$H_2O_2\ _l$ 50%	≈200-300	42	-44.84	12
$NaNO_2\ _c$	430	12,20	-85.9	12
	320	43		
$NaNO_3\ _c$	557	12,20	-111.54	12
	380	43	-101.54	14
$NaN_3\ _c$	270-365 in vacuum	56	-5.08	15
$Na_2Cr_2O_7 \cdot 2H_2O\ _c$	400	20	----	--
$NaMnO_4 \cdot 3H_2O\ _c$	170	20	----	--
$KNO_3\ _c$	561	12	-117.76	12
	400	43		
$KClO_4\ _c$	580-585	46	-103.22	38
	470-580	55	-102.8	18
			-103.6	12
$K_2S_2O_8\ _c$	≈100	13	-458.3	12
			-396.3	20
$KMnO_4\ _c$	273	54	-194.4	12
	≈240	13	-194.8	20
			-200	20
$Ba(NO_3)_2\ _c$	592-595	20	-229.7	20
			-237.1	12
$BaO_2\ _c$	---	--	-151.89	39
			-150.5	12
$Ba(ClO_4)_2 \cdot 3H_2O\ _c$	≈400	20,13	-405.4	12
	<420	49		
HOH* $_l$	---	--	-68.31	12
			-57.7 $_{gas}$	8
NaCl* $_c$	---	--	-98.23	12
			-92.23	18

(a) assuming amorphous carbon
* corresponds to reference materials

subscript following material composition corresponds to material phase:
c = crystal   l = liquid

Unless otherwise stated heats of formation, combustion, polymerization, decomposition, and explosion are given in kcal/mole.

The (p) or (v) symbol before the thermochemical data corresponds to values obtained under constant pressure or constant volume conditions.

Table 6 (Cont.)

THERMOCHEMICAL DATA

Material	Heat of		Reference(s)
NH_4NO_3 c	Formation	-87.3	13,14,15,20
		(v) -84.5	15
		(p) -88.1	15,20
		-1098.4 cal/gm calculated	21,26
	Combustion	(v) 50.3 calculated	15,20
		346.0 cal/gm	15,26
	Decomposition	33.14	15
		25.86	15
		(p) 29.5	15,20
	Explosion	346 cal/gm	15,26

Hazards: AN can deflagrate above 325°C. If confined, AN can explode above 250°C. AN is known to decompose at 170°C, but possible decomposition as low as 100°C[15,17]. Incidents of AN explosions and fires can be found in references 15 and 17.

Material	Heat of		Reference(s)
NH_4ClO_4 c	Formation	-69.42	13
		-70.74	27
		-79.7	17,20
		-665 cal/gm	15,26

Hazards: At 350°C the thermal decomposition of NH_4ClO_4 approaches 20% as determined by DTA[41]. NH_4ClO_4 used as an explosive ingredient of mixtures in pyrotechnics and as projectile filler[17]. Classified as an oxidizing material by DOT.

Material	Heat of		Reference(s)
Hydrazine l	Formation	13.8	17
		12.05	12,13,17,20
		12.10	18
	Combustion	148.6	20
Hydrazine. H_2O l	Formation	8.16	13
		10.3	17
		10.2	20

Hazards: Anhydrous hydrazine burns vigoursly in air and is of interest as a possible rocket fuel[28]. Both the hydrate and the anhydrous material are readily susceptible to atmospheric oxidation. Hydrazine can be decomposed by an electric spark and also by ultra-violet irradiation. Hydrazine has been reported to undergo slow, spontaneous decomposition into hydrogen, nitrogen and ammonia[28,53].

Material	Heat of		Reference(s)
Acetaldehyde l	Formation	-45.9	34
		-39.76_{gas}	12,13,14
		(p) -47.9	15
	Combustion	279.0	13
		(p) 281.9	15

Hazards: Mixtures of acetaldehyde vapor with air (4-57%) are highly flammable and explosive. Acetaldehyde explosive hazard is also severe when exposed to flame[15,21].

Table 6 (Cont.)

THERMOCHEMICAL DATA

Material	Heat of		Reference(s)
m-Dinitrobenzene $_c$	Formation	-6.2	34
		-19.2 (a)	17
		-24.2 (a)	17
		-8.6 (a)	17
		-5.2 @18°C	14
	Combustion	(v)699.4	15
		(v)698,4160 cal/gm	15
		696.8	13
		(p)699.8,4155 cal/gm	15
	Explosion cal/gm	(v) 870	15

Hazards: Explodes when heated to 580°C. Material does not detonate from exposure to heat up to 360°C.

Material	Heat of		Reference(s)
Trinitrobenzene $_c$	Formation	-21.1 (a)	17
		-25.8 (a)	17
		-23.0 (a)	17
	Combustion	663.7	13
		(v) 655.6	17
		(v) 659.6-665.9	15
		(v) 666.1	17
		(v) 3096cal/gm @17°C	15
	Explosion	1063cal/gm	15

Hazards: Classified by DOT as a high explosive.

Material	Heat of		Reference(s)
Acrolein $_l$	Formation	-17.79$_{gas}$	16
		-20.50$_{gas}$	14
		-27.97	14
		-29.17	34
	Combustion	398.6	13,16
		(v) 391.5	14
		6.95 kcal/gm	16

Hazards: Classified as a flammable liquid[1]. Tends to dimerize on heating[16].

Material	Heat of		Reference(s)
Ethyl Nitrate $_l$	Formation	-45.7	24
		-37.0$_{gas}$	24
		-44.3	12
	Combustion	322.4	13
		324.0	23
	Explosion oxygen free conditions	77.6, 853 kcal/kg	23

Hazards: Ingredient of liquid rocket fuels. Decomposition of ethyl nitrate in the gaseous phase has been studied in the temperature range 161-201°C. The main decomposition product is ethyl nitrite. By-products include methyl nitrite, nitromethane, nitrogen dioxide and nitrous oxide[17].

Table 6 (Cont.)

THERMOCHEMICAL DATA

Material	Heat of		Reference(s)
Nitromethane $_l$	Formation	-21.28	13,14
		-27.03	17,19
		-17.86_{gas}	17
	Combustion	169.4	13,17,19

Hazards: Nitromethane under pressure can burn as a monopropellants. NM has a 50% probability of becoming sensitive to a #8 blasting cap at (54.5-60°C)[19]. Liquid NM can explode when heated under confinement to near its critical temperature (315°C). Incidents such as fires and explosions attributable to NM can be found in references 17, 25, and 58.

Material	Thermochemical Data-Heat of		Reference(s)
Styrene-monomer $_l$	Formation	24.72	35
		35.32	13
		35.11_{gas}	35
		35.22_{gas}	12
	Polymerization	8.0-9.5	40
		13.8	40
		17.4	29
		160.2 cal/gm	34
		69.79 int k joule	30
	Combustion	1050.4	34,35
		1060.9_{gas}	12
		1047.1	13
		10.086 kcal/gm	34
		(p) 780.98 kg cal/mole	36
		4394.88 int k joule	30
	Decomposition Temperature	310-350°C	34
Guanidine Nitrate $_c$	Formation	-93.0	51
		-91.1	14
Chloropicrin $_l$	Formation	-26.7	57
Crotonaldehyde $_l$	Formation	-34.45	34
	Combustion	542.1	13
m-Dinitrophenol $_c$	Formation	-55.5	34
	Combustion	648.0	13
Acrylonitrile $_l$	Formation	35.9	34
	Polymerization	17.3	16
	Combustion	420.5	16
		7925 cal/gm	16
1,1 Dimethyl-hydrazine $_l$	Combustion	3580 kcal/kgm	17

Table 7

Thermal Stability Summary

Material	% Decomposition	Gas Evolution mm/mg	Threshold Initiation Temperature °C
Acetaldehyde	80	9.6	---
Acrolein	100	9.3	(a)
Acrylonitrile	100	1.7	710
Ammonium nitrate	100	41.1	---
Chloropicrin	100	(b)	325
Crotonaldehyde	88	7.5	780
30%-Hydrogen peroxide	100	14.9	(c)
m-Dinitrophenol	100	41.0	470
Ethyl nitrate	100	36.9	375
Guanidine nitrate	100	8.6	(d)
95% Hydrazine	100	(e)	615
85% Hydrazine hydrate	100	7.5	625
1,1-Dimethylhydrazine	100	6.6	515
Potassium persulfate	---	6.2	---
Potassium permanganate	100	13.5	---
Nitroglycerine*	100	---	220
Nitromethane	10	4.7	370
Sodium permanganate	100	14.5	---
Styrene-monomer	(f)	0.0	(g)
Trinitroanisole*	100	54.0	411
Trinitrotoluene*	100	47.6	427

(a) No threshold initiation temperature. Maximum temperature 748°C.

(b) Gas produced by chloropicrin decomposition reacts with mercury in manometer.

(c) H_2O_2 reacts with stainless steel tubing.

(d) Decomposes at melting point.

(e) Total volume of gas produced seems to depend on the amount of ullage air.

(f) 100% polymerization.

(g) No threshold initiation temperature. Maximum temperature 818°C.

---

* reference materials

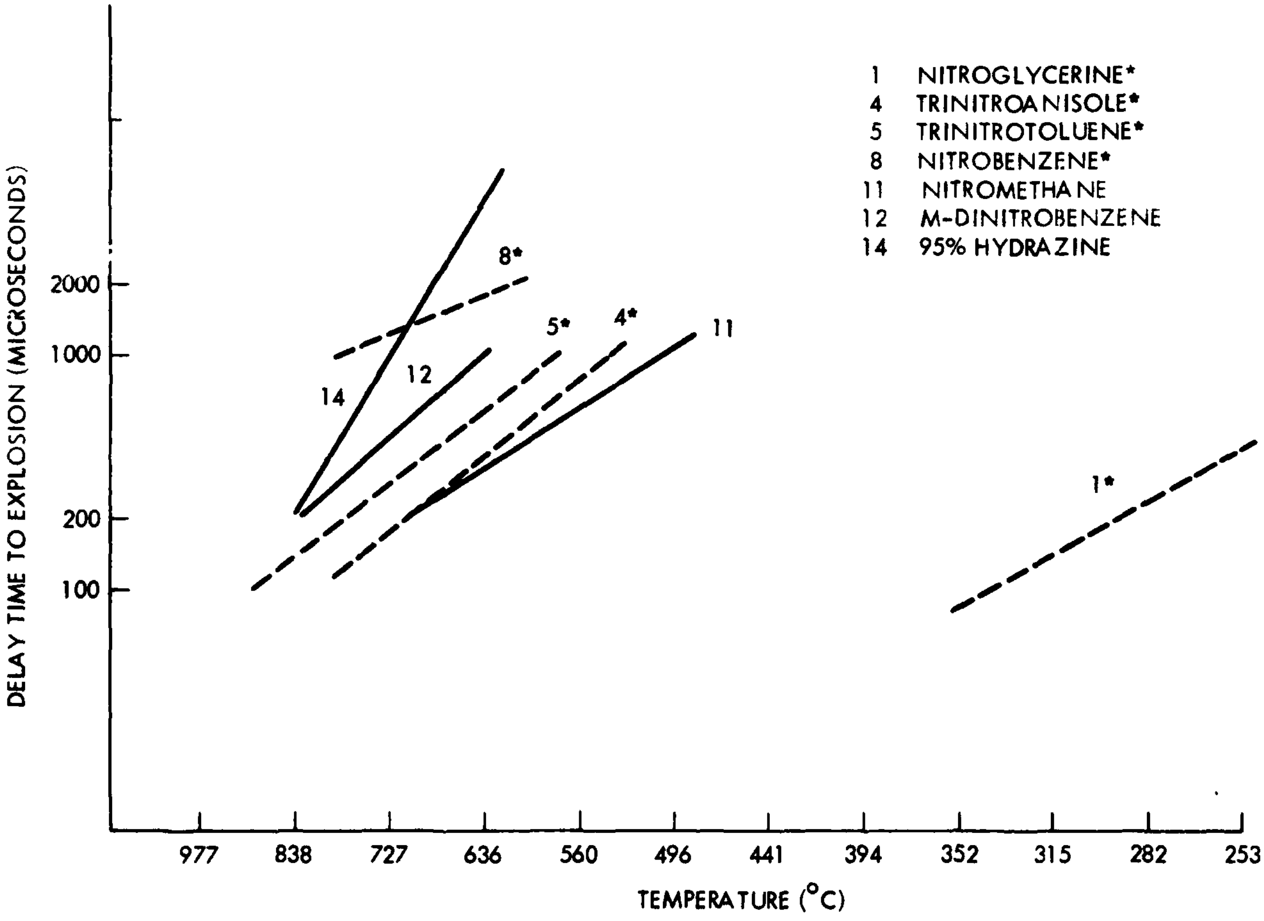

FIG. 1 THERMAL SURGE DATA

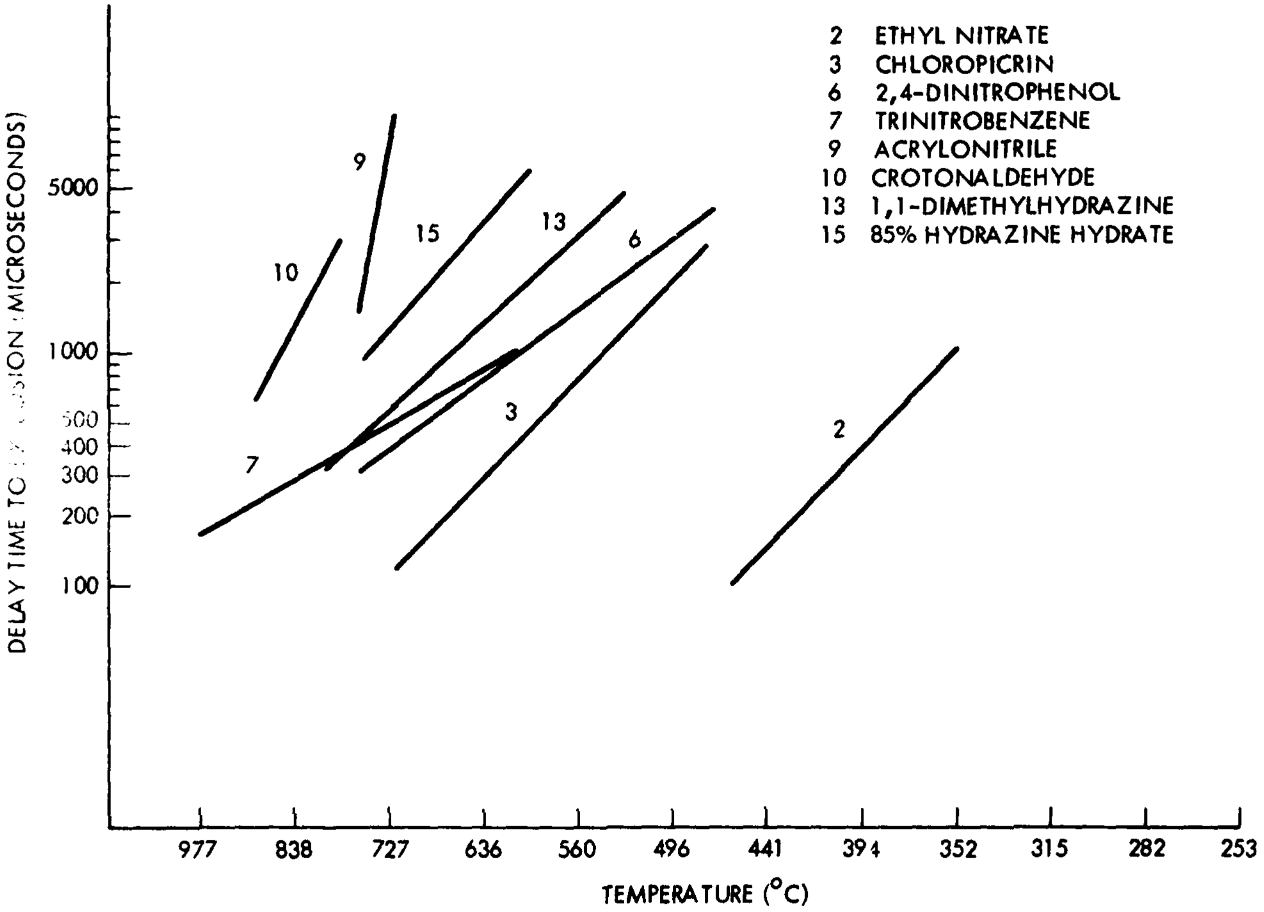

FIG. 1 THERMAL SURGE DATA

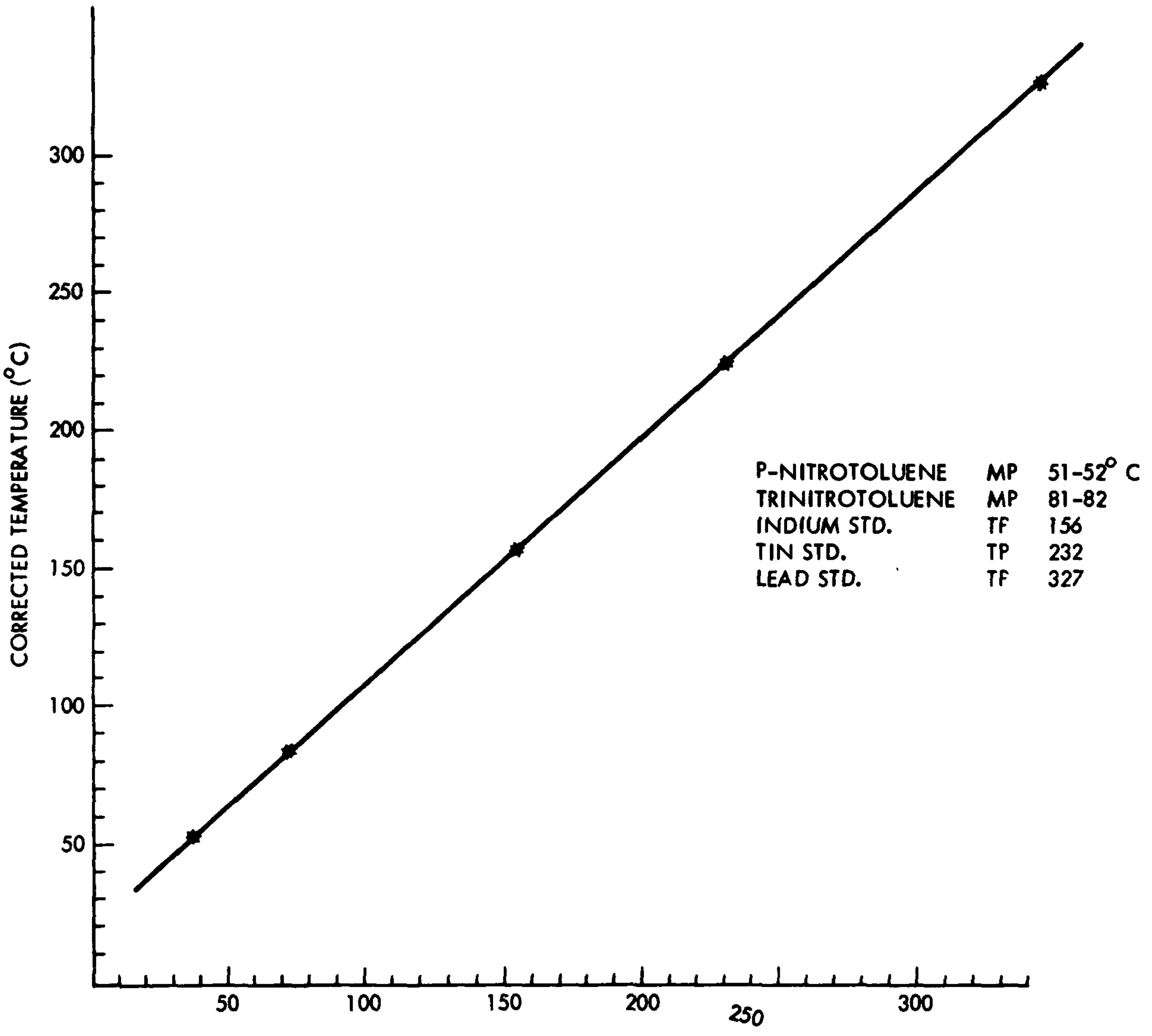

FIG. 2 DSC TEMFERATURE CORRECTION GRAPH

U-TYPE MANOMETER & SAMPLE TUBE

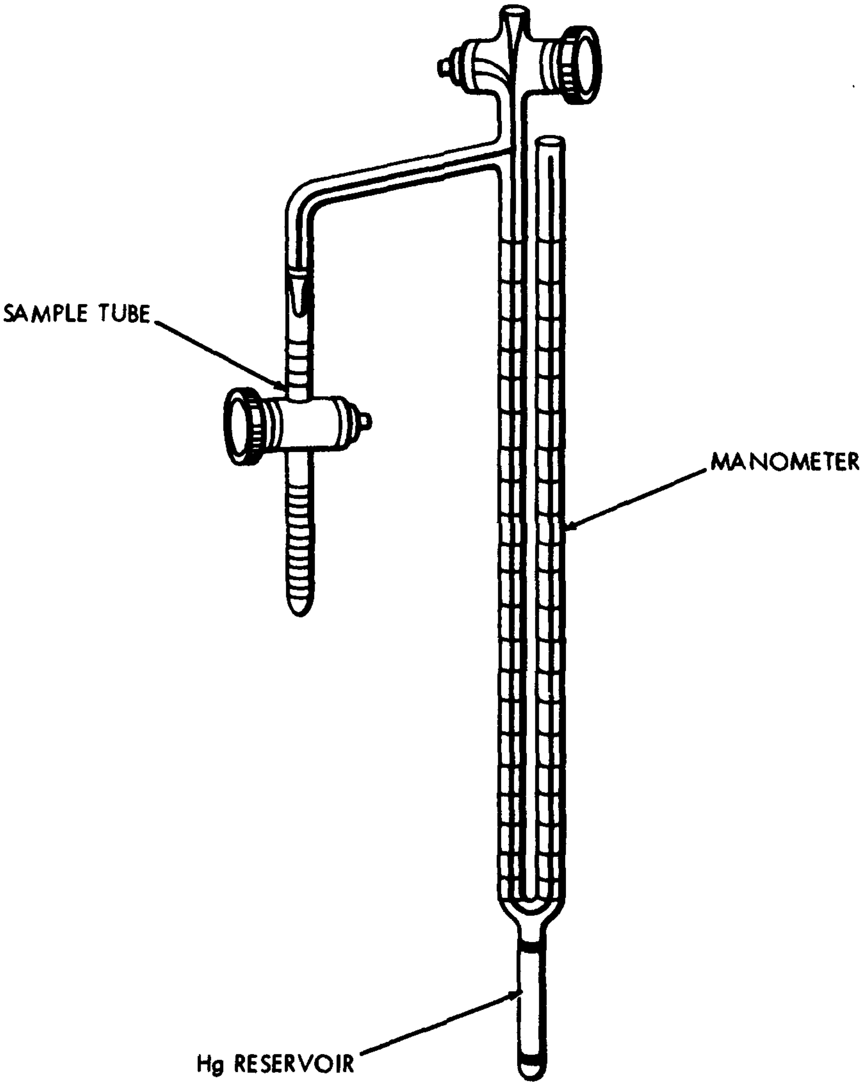

FIG. 3 GAS EVOLUTION APPARATUS

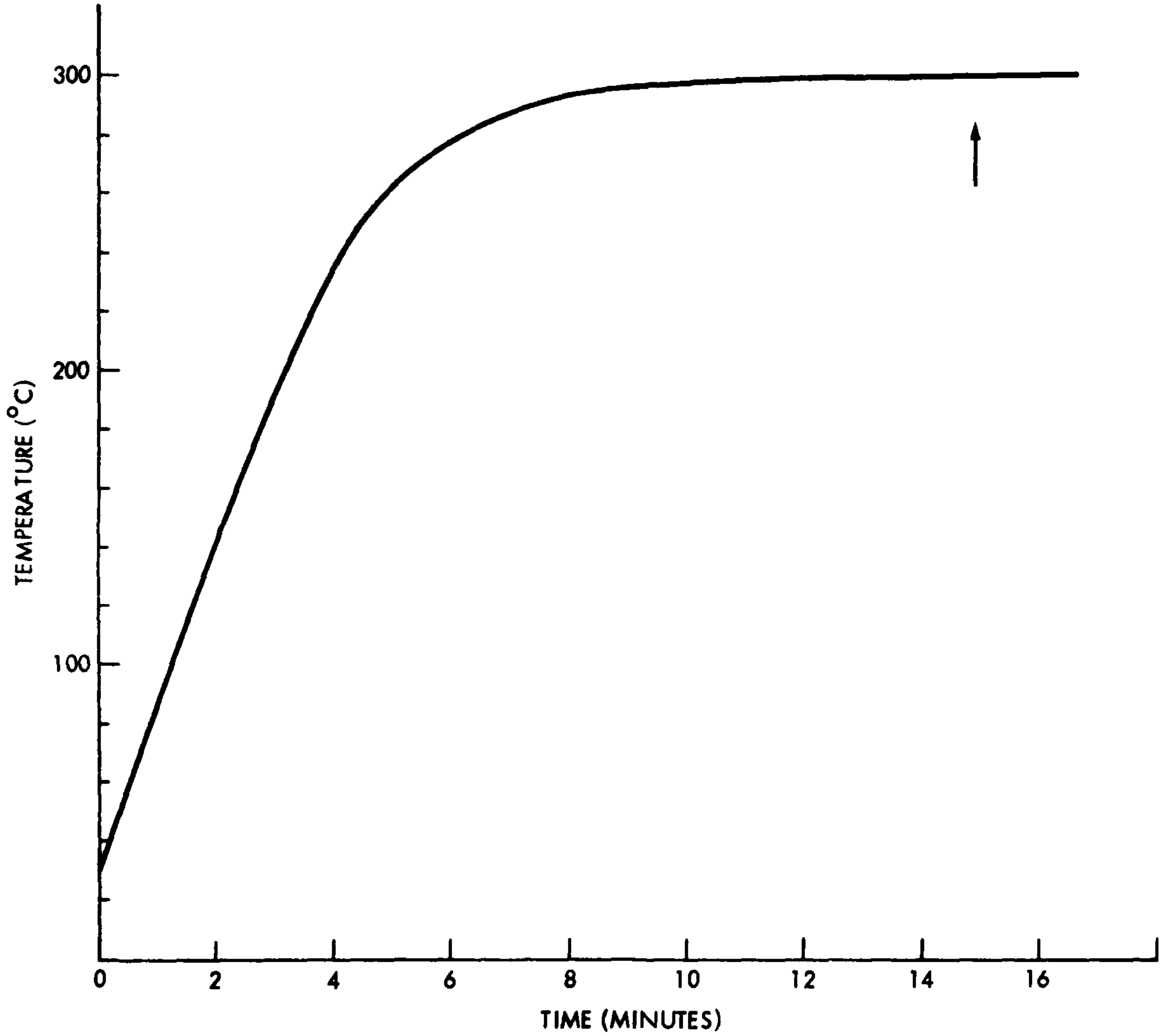

FIG. 4 SAMPLE HEATING RATE

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