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THERMAL PROPERTIES
&
CHEMICAL REACTIVITY

L. C. Myers

DEVELOPMENT DIVISION

January, February, March 1971
SANL 804-007

For
Lawrence Radiation Laboratory
Livermore, California

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THERMAL PROPERTIES & CHEMICAL REACTIVITY

L. C. Myers

DEVELOPMENT DIVISION

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The objective of this project is to determine the thermal and chemical reactivity properties of explosives, and to continue the development and evaluation of useful thermal tests.

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ABSTRACT

Two coupon test samples containing LX-09/Sylgard/Mulberry and LX-10/Sylgard/Mulberry were disassembled for evaluation. Thermal analysis data for the explosives and the analysis of the atmosphere are reported. Identification of several components in the atmosphere was made.

The problems associated with the analysis of LX-09 for FEFO by gas chromatography are discussed and the data from the analysis of two specially prepared samples of "LX-09" are reported.

The data for a series of standard and modified Henkin time-to-explosion for PETN are reported. The modified time-to-explosion runs are first cooled for a fixed time, preheated for 40 to 80 seconds, recooled for a fixed time and then reheated until the sample explodes.

A 0.42 cc liquid sample was trapped during the pump out of the W-68 AAU and a preliminary analysis of the sample is reported.

The analysis of the atmosphere in the first samples from the PASS A LX-09 evaluation program is reported.

DISCUSSION

COUPON TEST SAMPLES

Two coupon test samples were disassembled after thermal aging for 22 months at 80 C. Sample TS-23 was LX-10/Sylgard/Mulberry, Sample TS-27 was LX-09/Sylgard/Mulberry (both were in a helium atmosphere).

Sylgard in both assemblies was in very good condition but the Mulberry in Sample TS-27 was oxidized.

The atmosphere of both containers was analyzed by mass spectrometry, but the spectra were very complex and only a partial analysis could be made. Table I gives an analysis of the major components in the atmosphere.

A portion of the atmosphere was fractionated using cold traps then analyzed by gas chromatography/mass spectrography. This analysis showed Sample TS-23 contained traces of trimethylfluorosilane and an unidentified component with a mass of 147 and 151.

Sample TS-27 showed traces of water, methanol, dimethyldifluorosilane, methyl formate trimethylfluorosilane, acetone, ethyl formate, nitromethane and

Table I Analysis of the Atmosphere in Coupon Test Samples
TS-23 and TS-27

	Sample TS-23 LX-10/Sylgard/Mulberry (%)	Sample TS-27 LX-09/Sylgard/Mulberry (%)
H ₂	0.23	8.48
HE	68.20	44.75
N ₂	8.53	28.07
O ₂	1.14	0.05
Ar	0.11	0.30
CO ₂	0.99	5.96
N ₂ O	5.86	10.32
Acetone	0.76	0.12
Total %	85.82	98.05

acetic acid, as well as other components having a mass of 133, 151, 207, 230, 281, and 284. The 8.48% hydrogen probably resulted from the oxidation of the Mulberry.

The chemical reactivity test data for the LX-10 and LX-09 from Samples TS-23 and TS-27, and controls are given in Table II.

Table II Chemical Reactivity Test Data for LX-10 and LX-09
(μ l of gas evolved corrected to STP)

	N ₂	CO	NO	CO ₂	N ₂ O	Total
LX-10 Control	11.9	< 1	< 1	2.23	2.59	16.7
LX-10 TS-23	16.83	< 1	< 1	6.24	8.28	31.4
LX-09 Control	9.33	1.03	21.32	12.27	5.84	49.8
LX-09 TS-27	9.25	1.12	14.18	9.27	5.35	39.2

The DTA thermograms show no significant differences in the controlled and thermally aged LX-10 and LX-09 from Samples TS-23 and TS-27, respectively.

ANALYSIS OF FEFO IN LX-09 BY CHROMATOGRAPHY

For several years Pantex has conducted many small scale thermal aging studies on LX-09 alone and in contact with other materials. Various thermal tests such as DTA, EGA, DSC, TGA, Henkin Time-to-Explosion, and the chemical reactivity test were used to detect differences between the controlled and thermally aged samples of LX-09. TGA thermograms of some of the aged LX-09 samples showed change in rate of weight loss which could have resulted from a change in composition. The standard compositional analysis has the disadvantage that it gives the amount of fluorine in the sample and does not give any indication as to the condition of the FEFO. Thus, there was a need for a method to determine small changes in the amount of FEFO in LX-09.

Some preliminary work (1) indicated that the analysis of LX-09 for FEFO by gas chromatography was possible but some refinements would be needed to improve the accuracy.

In the first attempts to use this method, the N-butyl ether was chosen as the internal standard. With the N-butyl ether it was necessary to use temperature programming; and for mixtures of N-butyl ether, FEFO and chloroform the area of FEFO peak was dependent on the temperature programming rate. As the programming rate was decreased the area of the FEFO peak decreased. This was observed only in the three-component system. If any two components were mixed the peak area was independent of heating rate. Therefore, it was assumed that there was a compatibility problem in this three-component system.

Dinitrobenzene was selected for the internal standard because it was soluble in chloroform, could be chromatographically separated from chloroform and FEFO using OV-3 on Chromosorb W HP, and the peak areas were essentially independent of programming rate.

A second problem was the reproducibility of the ratio of areas of the DNB peak to the FEFO peak. Variations of as much as 20% were obtained but this was corrected by diluting the sample with more chloroform. A satisfactory ratio is 4 mg of DNB, 20 mg of FEFO to 50 ml of chloroform. The ratio of 4 mg of DNB to 20 mg FEFO gives a ratio of the peak areas of approximately one.

New standards should be made up daily because there is a small increase in the peak area ratio of DNB to FEFO from day to day. The cause of this change is not known. If the operating temperatures and flow rates are not changed the product of the ratio of the weight of FEFO to DNB and the peak area ratio of DNB to FEFO varies less than 0.3% in a period of two weeks.

The gas chromatograph used for these analyses was a Hewlett Packard Model 5750-B equipped with a dual-flame ionization detector. A Datex digital integrator model DIR-1 was used to measure peak areas. The columns were

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(1) *Pantex Quarterly*, January, February, March 1970.

10% OV-3 on Chromosorb W, HP (80/100 mesh) packed in a 1/8-inch OD by 1-meter stainless steel tubing. Sample injection was with a 10 μ l Hamilton syringe.

The columns were conditioned at 300 C for 1 to 2 hours after 15 to 20 samples had been run. The temperature of the oven, injection parts and flame ionization detector were 150, 180, and 300 C, respectively. Flow rates for helium, hydrogen and air were 50, 10, and 400 cc/minute, respectively. Five μ l samples were injected.

A standard equivalent to 2% FEFO in a 10 g sample of LX-09 was prepared by dissolving 40 mg of dinitrobenzene and 200 mg of FEFO in 500 ml of chloroform (all weights were to 0.01 mg). The "unknown" LX-09 samples were prepared by mixing 9.40 g of HMX, 0.40 g of DNPA and 0.20 g of FEFO with 0.040 mg of DNB. This mixture was added to 500 ml of chloroform.

The amount of FEFO in "unknown" LX-09 samples was calculated by:

$$\text{Wt. of FEFO in unknown} = \left(\frac{\text{Wt. of FEFO in Standard}}{\text{Wt. of DNB in Standard}} \right) \left(\frac{\text{Ratio of Peak Areas of DNB to FEFO for Standard}}{\left(\frac{1}{\frac{\text{Ratio of Peak Areas of DNB to FEFO for Unknown}}{\left(\text{Wt. of DNB in Unknown} \right)} \right)} \right) \quad (1)$$

The results for a standard and two "unknown" LX-09 samples are given in Table III.

The mathematical uncertainty of equation (1) was evaluated for the following conditions:

$$(a) \quad \frac{\text{Wt. of FEFO in Standard}}{\text{Wt. of DNB in Standard}} = 5.0 \pm 0.025$$

$$(b) \quad \frac{\text{Area for DNB in Standard}}{\text{Area for FEFO in Standard}} = 1.0 \pm 0.005$$

$$(c) \quad \frac{\text{Area for FEFO in Unknown}}{\text{Area for DNB in Unknown}} = 1.0 \pm 0.005$$

$$(d) \quad \frac{\text{Wt. of DNB in Unknown}}{\text{Wt. of DNB in Unknown}} = 40 \pm 0.01$$

The uncertainty of the weight of the FEFO is less than 1.1% which equals to 0.022% of the percentage of FEFO in LX-09. The major uncertainty is in the ratio of peak areas.

Table III Analysis of FEFO in LX-09 by Gas Chromatography

	Sample A (g)	Sample B (g)	Sample C (g)
DNB	0.04117	0.03091	0.03130
FEFO	0.24956	0.20605	0.20293
DNPA	-0-	0.34152	0.39233
HMX	-0-	9.43469	9.60182

Run	Ratio of DNB to FEFO		
1	1.1519	1.0327	1.0647
2	1.1584	1.0239	1.0662
3	1.1591	1.0309	1.0642
4	1.1601	1.0468	1.0841
5	1.1458	1.0486	1.0842
6	1.1558	1.0468	1.0745
7	1.1531	1.0369	1.0796
8	1.1534		
Ave	1.1547	1.03809	1.07393
1 σ	0.0047	0.0095	0.0089

% FEFO (calculated from GC)	2.09	2.00
% FEFO	2.06	1.99

MODIFIED HENKIN TIME-TO-EXPLOSION FOR PETN

A series of modified Henkin time-to-explosion (TE) tests were run with PETN. The modified runs consist of cooling the sample, preheating for a fixed period of time, recooling, and then heating the sample until it explodes. Table IV gives runs at 171 C with preheating times of 40 and 80 seconds. The 40-second preheat period made very little difference in the TE, while there was a significant change in the TE with an 80-second preheating period; although there was approximately 16 out of 19 samples which failed to explode. Those caps which failed to explode showed evidence of leaking. The PETN had melted and leaked past the gas check and lead plug.

A series of standard TE was run with PETN for comparison. The TE is given in Table V and a plot of the log of the TE as a function of the reciprocal of absolute temperatures is given in Fig. 1.

Table IV Modified Time-to-Explosion for PETN

	Temperature (C)				
	<u>0</u>	<u>171</u>	<u>0</u>	<u>171</u>	<u>Total Time</u> <u>@171</u>
	<u>Time (sec)</u>				
Control Runs	120			137	137
PETN	120			150	150
	120			NG	-
	120			141	141
	120			141	141
	120			142	142
	120			123	123
	120			140	140
	120			128	128
Harmonic Mean				(137)	(137)
Modified Runs	120	40	120	NG	-
PETN	120	40	120	128	168
	120	40	120	137	177
	120	40	120	146	186
	120	40	120	101	141
Harmonic Mean				(126)	(166)

	Temperature (C)				
	<u>0</u>	<u>171.5</u>	<u>0</u>	<u>171.5</u>	<u>Total Time</u> <u>@171.5</u>
	<u>Time (sec)</u>				
Control Runs	120			250	250
PETN	120			129	129
	120			124	124
	120			126	126
Harmonic Mean				(144)	(144)
Modified Runs	120	80	120	59	139
PETN	120	80	120	79	159
	120	80	120	101	181
Harmonic Mean				(76)	(158)

Table V Time-to-Explosion for PETN

Temperature (C)	<u>171</u>	<u>177</u>	<u>184</u>	<u>191</u>
	Time (sec)			
	125	75	38.5	23
	131	73	41	22
	129	71	40	26
		75		
		73		
		74		
Harmonic Mean	(128)	(73)	(40)	(23.5)

Fig. 1. Time-to-explosion for PETN

ANLAYSIS OF SAMPLE FROM THE W-68 AAU

Two liquid samples which were collected in a -126 C trap during the pump out of the first W-68 AAU were analyzed. These two samples were combined to give a total volume of 0.42 cc with a vapor pressure of 3.26 cm at 22 C (as measured with a mercury manometer).

A mass spectrum (Fig. 2) shows those mass peaks which are 1% or more of the 43 peak; above mass 100 there were peaks at 112, 117, 119, 121, 130, 131, 132, 133, 134, 149, 164, 168, and 207, which was less than 1% of 43 peak.

A few μ liters of the liquid were chromatographed using a 1/8-inch OD by 12-foot long Porapak Q packed column which was programmed from -100 to 175 C and held at 175 C for 20 minutes. A mass spectrometer connected in series with the gas chromatograph was used to identify each peak. Results of this analysis are given in Table VI.

Table VI Analysis of the Liquid Sample From W-68 AAU

	<u>Approximate % Relative to Water</u>
Water	100.00
Methanol	0.05
Ethanol	0.30
Acetone	3.00
Isopropyl Alcohol	0.30
Trimethylfluorosilane	Trace
Xylene	Trace

The liquid sample was fractionated using traps at -23, -44, -90, -123, and -96 C. The analysis of the -23 C trap (by mass spectrometry) shows xylene and other components which have not been identified. The xylene accounts for the mass peaks at 105 and 106.

Analyses of the -44, -90, -123, -196 C traps have not been completed.

Fig. 2. Mass spectrum of vapor from the W-68 AAU sample.

PASS A LX-09 EVALUATION PROGRAM

LRL has requested that Pantex evaluate the chemical and mechanical properties of LX-09 in a PASS A thermal environment. A total of 125 tension and 69 compression specimens were sealed in stainless steel containers. Free space in the containers was reduced to a minimum with glass beads. The containers were evacuated and approximately half were filled with a mixture of N_2 , O_2 and CO_2 (ratio of 60/30/10, respectively), and the others were filled with dry N_2 . In September 1969, the containers were then placed in the PASS A chamber, and samples scheduled to be taken at 1-, 2-, 4-, 6-, and 8-year intervals.

Although several problems were encountered, gas analysis of both atmospheres (N_2 and $N_2/O_2/CO_2$) from the tension specimen containers has been completed. The first samples were lost because the gas burette was too small and a larger burette had to be built, and later another sample was lost because of a pin hole leak in the gas transfer pump. Also, several samples were lost because the mass spectra could not be interpreted even after the samples were fractionated using traps cooled at -196, -123, and -78 C.

Successful analysis of the atmosphere was made using mass spectrometry on the fraction coming through the liquid nitrogen trap and gas chromatography for those fractions collected in the traps. The components identified by gas chromatography account for a majority of the mass peaks in the spectra which could not be interpreted. The analysis of the atmosphere is given in Table VII. Sample No. 7 is believed to be a leaker because the ratio of N_2 to O_2 and argon indicates the presence of air. This would also account for the larger volume of gas. The presence of trichlorofluoromethane in the samples has not been explained. After the mechanical testing, a complete thermal and composition analysis will be made on some of the broken specimens.

Table VII Analysis of the Atmosphere for PASS A LX-09 Samples

	N ₂ /O ₂ /CO ₂ (60/30/10)				N ₂ (100%)			
	Sample #7		Sample #9		Sample #6		Sample #8	
	ml @ STP	%	ml @ STP	%	ml @ STP	%	ml @ STP	%
N ₂	92.90	75.56	46.37	58.44	75.92	95.71	75.37	96.61
O ₂	26.45	21.51	20.89	26.33	0.095	0.12		
CO								
NO					0.690	0.87	0.518	0.66
CO ₂	4.504	3.66	8.093	10.20	1.742	2.20	1.336	1.71
N ₂ O	0.319	0.26	1.884	2.37	0.455	0.57	0.403	0.52
Ar	1.09	0.89						
Acetone	1.777	1.45	0.326	0.42	0.278	0.35	0.157	0.20
H ₂	0.109	0.08						
H ₂ O	0.7497	0.61	0.352	0.44	0.107	0.13	0.14	0.18
Methanol	0.0104	0.008	0.096	0.12	0.001	0.001	0.012	0.01
Trichlorofluoromethane	0.0474	0.03	0.239	0.30	0.0371	0.047	0.081	0.10
Total	122.950		78.250		79.3300		78.017	

FUTURE WORK, COMMENTS, CONCLUSIONS

Coupon test samples containing LX-10/Sylgard/Mulberry and LX-09/Sylgard/Mulberry were disassembled after 22 months at 80 C in a helium atmosphere. The Sylgard was in good condition; the Mulberry with the LX-09 was oxidized more than the sample with LX-10.

Traces of some fluorosilane were detected which indicate that the FEFO in the LX-09 is reacting with the Sylgard. A majority of the trace components in the atmosphere have been tentatively identified and standards have been ordered for verification. Therefore, the analysis of the atmosphere in the next series of samples should be much more complete.

The source of the trimethylfluorosilane in Sample TS-23 is not yet explained. The only source of fluorine is the Viton in the LX-10.

The thermal analysis tests which have been completed show no significant differences in the control samples and LX-10 and LX-09 from the coupon assembly. Additional thermal tests will be run in the near future.

The analysis of FEFO in LX-09 by gas chromatograph is showing improvement. By using dinitrobenzene (DNB) for the internal standard the reproducibility of the ratio of the areas of DNB to FEFO in a chloroform solution is better than 0.5%.

The analysis of FEFO in two prepared samples containing HMX, DNPA, and FEFO was 2.09 and 2.00% when the actual amount of FEFO was 2.06 and 1.99%, respectively.

The mathematical uncertainty of this technique was evaluated using estimates of the accuracy of each measurement; the uncertainty of the percentage of FEFO in LX-09 was determined to be $\pm 0.022\%$. The largest error is in the ratio of the peak areas of DNB to FEFO.

In PETN Henkin tests, at 171 C, a 40-second preheat period had an average time-to-explosion less than the control, but the scatter in the data makes it difficult to determine if this was significant. An 80-second preheat period reduced the time-to-explosion.

The gas chromatography/mass spectrometry analysis of the liquid collected from the W-68 AAU showed water, methanol, ethanol, acetone, isopropyl alcohol, and a trace of trimethylfluorosilane and xylene. There are other components which have not been identified.

The liquid was fractionated using traps at -23, -44, -123, and -196 C, and a complete analysis of each trap will be made in the near future.

Analysis of the atmosphere in the first series of samples from the PASS A LX-09 evaluation program has presented a number of problems. A special size of gas burette had to be built so that the volume of gas could be measured. The atmosphere contained traces of many components which made the interpretation of the mass spectrum impossible; therefore, it was necessary to fractionate using cold traps at -78, -123, and -196 C. The fraction which passed through all three traps was analyzed by mass spectrometry and the contents in each trap analyzed by gas chromatography.

There was a small amount of trichlorofluoromethane in every container, and its source has not been determined. An analysis will be made on the cylinder of $N_2/O_2/CO_2$ to see if it has a trace of trichlorofluoromethane.