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A STUDY OF THE EFFECTS OF NUCLEAR RADIATION ON ORGANIC EXPLOSIVES*

MASTER

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ABSTRACT

Samples of six explosive compounds (TNT, tetryl, NC, RDX, HMX, PETN) and four explosive mixtures were exposed to the neutron (and gamma) radiation from a power reactor at integrated flux levels of approximately 10^{15} n/cm.² (5×10^6 r.), and 3×10^{16} n/cm.² (2×10^8 r.). The irradiated samples were subjected to a variety of chemical and physical tests. Only minor effects of the radiation were noted at the lower exposure level, but extensive deterioration of the aliphatic and heterocyclic compounds occurred in the 10^{16} run. G-values of 2.9 and 1.4 were obtained for the destruction of RDX and HMX, respectively.

An experiment also is briefly described in which samples of five explosive compounds and mixtures were exposed to a radiation burst from the Los Alamos critical assembly known as Godiva II. Although the total dose received by the samples in this experiment was quite low ($\sim 7 \times 10^{12}$ n/cm.²), the peak flux was quite high ($\sim 10^{17}$ n/cm.²/sec.). No significant damage to the samples resulted from this exposure.

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INTRODUCTION

The effects of nuclear radiation on various materials is a subject of considerable current interest from both the research and engineering points of view. This is true in the case of explosives as well, and, indeed, several unusual questions arise in connection with radiation damage studies on explosives because of the special properties of this class of materials.^{1,2}

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¹ F. P. Bowden and A. D. Yoffe, "Fast Reactions in Solids," Academic Press, Inc., New York, N.Y., 1958, Chapter VII.

² A Discussion of the Royal Society on "The Initiation and Growth of Explosion in Solids," Proc. Roy. Soc. A246, No. 1245, 29 July 1958.

In this paper we present the results of a preliminary study of the effects of the combined neutron and gamma radiation from a power reactor on ten organic explosive compounds and mixtures.

EXPERIMENTAL

Explosives. - The explosives used were obtained from military sources and, except as noted below, were tested as received. They are identified and briefly described as follows:

TNT - 2,4,6-Trinitrotoluene, crystalline, average particle size about 150 μ .

RDX - 1,3,5-Trinitrohexahydro-s-triazine, crystalline, 98% below 200 μ . This material contains about 6 to 7% HMX as a reaction by-product.

HMX - 1,3,5,7-Tetranitrooctahydro-1,3,5,7-tetrazocine, crystalline, average particle size about 250 μ . This material contains about 6 to 7% RDX as a reaction by-product.

Tetryl - 2,4,6-Trinitrophenylmethylnitramine, uniform spherical granules, average particle size about 0.5 mm.

PETN - Pentaerythritol tetranitrate, crystalline, fine needles.

NC - Nitrocellulose, 11.8% N.

Composition B - 60/40-RDX/TNT. This material was received in the form of small cast pellets. These were ground, and the material passing a No. 10 U.S. Standard Sieve was used. The particle size ranged from several millimeters (largest dimension) down to particles 100 μ or so in size.

9404 - 94/3/3-HMX/NC/tris(β -chloroethyl)phosphate. Contains 0.1% diphenylamine as stabilizer. This material was in the form of irregular granules 1 to 7 mm. in size.

9010 - 90/10-RDX/Kel-F 3700. Kel-F 3700 is a commercial chlorofluoropolymer available from the Minnesota Mining and Manufacturing Co., Inc. This material was in the form of roughly spherical granules 0.8 to 1.4 mm. in size.

9407 - 94/6-RDX/Exon 461. Exon 461 is a commercial chlorofluoropolymer available from the Firestone Plastics Company. This material was in the form of spherical granules approximately 0.3 mm. in size.

The last four materials are mixtures typical of those used in various military applications. Composition B is loaded by a melting and casting process. 9404, 9010, and 9407 are known generically as plastic bonded explosives and are processed by vacuum pressing techniques.

Irradiation Procedure. - Three gram samples of each explosive were sealed off in individual, evacuated quartz ampoules equipped with break-off seals and standard taper joints. In addition, 0.3" diam. x 1.25" long machined cylinders of cast Composition B and of pressed 9404, 9010, and 9407 were placed in similar unsealed containers. Each quartz container was then placed in a closed Dural cylinder designed to prevent external damage in the event any of the samples exploded during the test.

The samples were irradiated in the 3 Mw. Ground Test Reactor located at Convair, Fort Worth Division, Fort Worth, Texas. This reactor is basically a swimming pool type with a rectangular array of fuel elements and control rods measuring approximately 15" x 21" x 12" high. The reactor fuel is enriched uranium. The reactor is so arranged that, during irradiation experiments, samples may be placed within two feet of three sides of the core (identified for convenience as north, east, and west). Special exposure boxes were provided at these three locations by Convair and Sandia Corporation personnel to contain the samples. The boxes were equipped with temperature controls designed to maintain temperatures of either -80°F or +100°F. Thermocouples were used to monitor the temperature at various positions in the boxes, at the walls of some of the Dural and quartz containers, and at the surfaces of some of the explosive cylinders.

For the lower exposure level (hereafter referred to as the 10^{15} run), the reactor was operated at a power of 250 kw., producing a radiation flux at the sample location of about 6×10^{10} n/cm.²/sec. ($E_n > 1$ kev.) and 2×10^{12} γ /cm.²/sec. For the 10^{16} run, the reactor was operated at

full power, and the corresponding fluxes were approximately 3×10^{11} n/cm.²/sec. and 1.3×10^{13} γ/cm.²/sec.

During the irradiation experiments, the samples are separated from the reactor core by about 4" of water, 1" of aluminum, 1/4" of boral, and 12" of air, plus miscellaneous hardware associated with the exposure boxes and sample containers. By way of investigating the neutron energy spectrum in the exposure boxes, foil activation methods were used by Sandia Corporation personnel to obtain the following flux ratios:

$$\frac{\bar{\Phi} (E_n > 0.75 \text{ Mev.})}{\bar{\Phi} (E_n > 1 \text{ kev.})} = 0.82$$

$$\frac{\bar{\Phi} (E_n > 1.5 \text{ Mev.})}{\bar{\Phi} (E_n > 1 \text{ kev.})} = 0.38$$

$$\frac{\bar{\Phi} (E_n > 2.5 \text{ Mev.})}{\bar{\Phi} (E_n > 1 \text{ kev.})} = 0.19$$

These ratios imply that the fast neutron flux is primarily due to neutrons having energies between 0.75 and 2.5 Mev., and, indeed, the fast neutron energy spectrum does not appear to differ markedly from that of the unmoderated fission process.³ However, the dosimetry data given below

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³ S. Glasstone, "Principles of Nuclear Reactor Engineering," D. VanNostrand Company, Inc., Princeton, N.J., page 111.

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do indicate that slow neutrons contribute significantly to the total flux.

The γ flux exceeds the neutron flux by a factor of the order of 30, and is primarily due to photons having energies of the order of 1 Mev.

Dosimetry data were obtained by all three organizations participating in the test (LASL, Sandia, Convair). The LASL dosimeters were located inside the Dural containers, while the Sandia and Convair dosimeters were placed in nearby locations in the exposure boxes. The data obtained (averaged values) are given in Table I, and, using the above flux ratios, they may be summarized as follows:

Run	Integrated Neutron Flux, nvt ($n/cm.^2$)			γ Dose (r.)
	$E_n < 0.5$ ev.	$E_n > 1$ kev.	Est. Total	
10^{15}	1×10^{14}	7×10^{14}	$\sim 10^{15}$	5×10^6
10^{16}	4×10^{15}	2.6×10^{16}	$\sim 3 \times 10^{16}$	2.4×10^8

In the 10^{15} run, samples were placed in both the -80°F and the $+100^\circ\text{F}$ boxes. In the 10^{16} run, space was available to us only in one of the -80°F boxes. The temperatures recorded by the thermocouples in the 100°F box remained within several degrees of the nominal temperature, but difficulties with the controls on the cold boxes resulted in rather large temperature excursions in both runs. The temperature remained below -50°F in the 10^{15} run, but did get as high as room temperature (80°F) at times during the 10^{16} run. The -80°F figure thus has only qualitative significance, although at various places we will use the nominal temperature to identify the several sets of samples.

TABLE I

DOSIMETRY DATA FROM H.E. IRRADIATION RUNS (AVERAGED VALUES)

Run	Box	LASL		CONVAIR		SANDIA
		$\frac{n}{cm.^2}$ $E_n < 0.5 \text{ ev.}$	$\frac{n}{cm.^2}$ $E_n > 2.5 \text{ Mev.}$	$\gamma \text{ Dose (r.)}^a$	$\frac{n}{cm.^2}$ $E_n > 2.9 \text{ Mev.}$	$\frac{n}{cm.^2}$ $E_n > 2.5 \text{ Mev.}$
10^{15}	East +100°F	9.9×10^{13}	8.7×10^{13}	5.0×10^6	1.8×10^{14}	$\sim 2 \times 10^{14}$
10^{15}	West -80°F	9.8×10^{13}	1.1×10^{14}	5.2×10^6	1.4×10^{14}	$\sim 1 \times 10^{14}$
10^{16}	West -80°F	3.8×10^{15}	4.8×10^{15}	2.4×10^8	5×10^{15}	$\sim 5 \times 10^{15}$

^a From N_2O dosimeters, corrected for attenuation by Dural containers. Estimated reliability $\pm 35\%$.

It is worth noting that no evidence of significant γ heating of the quartz or Dural containers, or of the explosive cylinders, was indicated by the temperature measurements, and in no case do we have any cause to believe that purely thermal decomposition had a significant effect on the results.

Examination of the Samples. - After irradiation, the samples were returned to Los Alamos where they were subjected to a variety of chemical and physical tests. Because of the magnitude of this task, as well as other factors beyond our control, the examination of the samples began about one month after they had been irradiated and extended over a period of an additional nine months. This may have affected the results in some cases. In particular, the volume of evolved and trapped gases will change somewhat with time after irradiation,⁴ and also the samples

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⁴ J. V. R. Kaufman, Ref. 2, pp. 219-225. See also H. Rosenwasser, Oak Ridge National Laboratory report No. ORNL-1720, "Effects of Gamma Radiation on Explosives" (unclassified).

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of NC from the 10^{16} run continued to decompose at a rapid rate after irradiation had ceased. Where it appears useful to do so, the approximate time lapse between exposure and testing will be indicated.

The sealed tubes first were opened through the break-off seals on a vacuum system of known volume, and the volumes of gas present were determined in the usual way from the resulting P, V, T data. Samples of the gas were collected and analyzed on a CEC Model 21-103 mass spectrometer.

When the volume of decomposition products was small it was sometimes necessary to correct the volume and composition data for the air remaining in the tubes or trapped in the samples at the time the tubes were sealed off. This correction was based on the argon content of the gas. We note in passing that the modus operandi and sequence of steps involved in opening the tubes is such that those products (such as water and formaldehyde) present in the tubes as liquids were not measured and collected for analysis. This point is discussed at length later on.

After the tubes were removed from the vacuum line, the necks were broken off below the break-off seals, and the weights of the residues were determined by weighing the tubes before and after removing the samples and cleaning out the tubes (the weight losses of the machined cylinders were determined by direct measurement).

The samples were examined visually, and the densities of the cylinders were determined either from weight and dimensional data, or by the water immersion method. Crystal or particle densities were determined on both the irradiated and control samples of the granular materials by the sink/float method, using aqueous solutions of barium perchlorate as the suspension medium and a centrifuge to increase the sensitivity of the method.

The volume and composition of the gases trapped in the crystals were measured for some of the samples. A small quantity of a suitable solvent was frozen in the bottom of a tube of known volume. A 20 to 50 mg. sample of the explosive was then placed in the tube, and the tube was attached

to a vacuum line and pumped down. The tube was then allowed to warm to room temperature to dissolve the sample, the pressure rise was noted, and a sample of the evolved gas was introduced into the mass spectrometer for analysis.

Pyrolysis and differential thermal analysis curves were run on most of the samples. The technique for obtaining the pyrolysis curves has been described in detail elsewhere.⁵ The DTA curves were obtained with

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⁵ R. N. Rogers, S. K. Yasuda, and John Zinn, Anal. Chem. 32, 672 (1960).

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a small-scale adaptation of the usual technique, using samples of 20 mg. or less.⁶

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⁶ R. N. Rogers, Microchemical Journal, in press.

Other data obtained, or tests made, on many of the samples included the following: X-ray powder patterns, microscopic examination, melting points, elemental analyses, IR spectra, and paper chromatography. Conventional techniques and apparatus were used.

One additional test, peculiar to the explosives field, also was made on these samples. This is known as the drop-weight impact test, and is a test which is designed to measure the susceptibility of an explosive to accidental initiation, as by impact or friction. It is obviously a test of some importance in work with explosives. The general

procedure used in such tests, and some of the factors influencing the results, have been described by Bowden and Yoffe.⁷ The results obtained

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⁷ F. P. Bowden and A. D. Yoffe, "Initiation and Growth of Explosion in Liquids and Solids," Cambridge University Press, 1952.

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depend greatly on the method of measurement. The apparatus used at LASL has not yet been described in the literature. Briefly, 40 mg. samples of the explosive to be tested are placed on small squares of sandpaper, and these in turn are placed between two hardened steel cylinders. The lower cylinder is supported on a rigid base, and the upper cylinder is impacted by a free-falling, 2.5 kg. weight. The height of fall in centimeters (h) which produces explosions in 50% of the samples is estimated by the up-and-down method⁸ and is the reported sensitivity

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⁸ W. J. Dixon and A. M. Mood, J. Am. Stat. Assoc., 43, 109 (1948).

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index. The higher the 50% point, the less sensitive the explosive. The distribution of percent explosions is cumulative in the logarithm of the drop height, and hence the 50% point and standard deviation in log units (m and σ , respectively) also are reported and are used in statistical analyses of the sensitivity data.

RESULTS

Preliminary Observations. - The samples from the 10^{15} run showed very little in the way of externally visible changes. The changes in some of the 10^{16} samples, on the other hand, were quite striking. The colors of the aromatic compounds had changed considerably -- TNT, for example, changing from light yellow to dark brown. The color changes extended throughout the crystals. 9404 also changed in color, from blue to yellow, presumably because of chemical reactions involving the stabilizer. The pellets from the 10^{16} run changed color in a similar fashion and also were badly distorted. HMX, RDX, and PETN showed little external evidence of change, although all three underwent extensive chemical decomposition in this run.

The RDX sample from the 10^{16} run evolved a very strong odor reminiscent of a hydroxylamine derivative. The NC sample was evolving NO_2 (probably from NO plus air) at the time it was removed from the tube and continued to do so at an increasing rate. One portion of this sample has since deteriorated to a soft, foamy, transparent film. Another portion of the same sample is still in powder form (one year after irradiation) but is decomposing rapidly.

Weight, Density, and Dimensional Changes. - The losses in weight of the powdered samples are given in Table II. The weight, density, and dimensional data on the pellets, before and after irradiation, are given in Table III. In both cases the effects of the 10^{15} exposure are relatively minor, but most of the explosives tested underwent drastic changes as a result of the 10^{16} exposure.

Table II

Weight Losses of Irradiated Samples

Explosive	Weight Loss (%)		
	10^{15} (-80°F)	10^{15} (+100°F)	10^{16} (-80°F)
PETN	0.2	0.2	13.8
RDX	0.1	0.2	14.3
HMX	0.2	0.1	9.1
Tetryl	0.0	0.0	1.3
NC	0.4	0.9	9.0
TNT	0.3	0.2	0.3
9404	0.1	0.1	9.2
9010	0.1	0.1	11.8
9407	Meas. lost	Meas. lost	13.4
Comp. B	0.1	0.1	7.8

Table III

Dimensional, Density, and Weight Changes, Machined Cylinders

Explosive	Run	HEIGHT (inches)		DIAMETER (inches)		DENSITY (g./cc.)			WT LOSS (%)
		Before	After	Before	After	Before	After	Change	
Comp. B	10 ¹⁵ -80°F	1.2517	1.2530	0.3009	0.3013	1.723	1.711	0.012	0.5
Comp. B	10 ¹⁵ +100°F	1.2525	1.2552	0.3009	0.3015	1.723	1.706	0.017	0.3
Comp. B	10 ¹⁶ -80°F	1.2519	1.2732	0.3010	0.3200	1.721	1.433	0.288	10.9
9404	10 ¹⁵ -80°F	1.2493	1.2448	0.3017	0.3025	1.850	1.847	0.003	0.1
9404	10 ¹⁵ +100°F	1.2497	1.2472	0.3005	0.3008	1.850	1.847	0.003	0.1
9404	10 ¹⁶ -80°F	1.2493	1.2475	0.3007	0.3080	1.850	1.645	0.205	9.1
9010	10 ¹⁵ -80°F	1.2499	1.2515	0.3010	0.3015	1.783	1.772	0.011	0.1
9010	10 ¹⁵ +100°F	1.2498	1.2440	0.2990	0.3015	1.783	1.752	0.031	0.2
9010	10 ¹⁶ -80°F	1.2502	Warped	0.3010	Warped	1.783	1.212	0.571	13.3
9407	10 ¹⁵ -80°F	1.2503	1.2504	0.3008	0.3007	1.767	1.767	0.000	0.0
9407	10 ¹⁵ +100°F	1.2510	1.2530	0.3008	0.3006	1.766	1.762	0.004	0.1
9407	10 ¹⁶ -80°F	1.2500	Warped	0.3010	Warped	1.768	1.468	0.300	11.5

The results of the crystal or particle density measurements are given in Table IV. The reference values in this table are the commonly accepted crystal densities of the explosives listed. For the mixed explosives the values given for the control and irradiated samples are of relative significance only, as the granules of these materials commonly contain numerous internal voids not filled by the suspension medium.

Volume and Composition of Evolved Gases. - The available data are summarized in Tables V and VI (some of the gas samples were lost for various reasons). The compositions are reported only for the major constituents and hence the numbers do not, in general, add up to 100%.

NO_2 does not give a parent peak in the mass spectrometer, and hence any NO_2 present is included in the values given for NO. All the gas samples were examined on the vacuum line for evidence of the color of NO_2 , and in no case was any seen. For the higher pressure gas samples, this sets a fairly low upper limit on the amount of NO_2 which could have been present.

Volume and Composition of Trapped Gases. - These data are given in Table VII. For the 10^{15} run, data are reported only for HMX, as it had become clear by the time these measurements were made (9 months after irradiation of the samples) that the lower exposure level had produced only minor changes in the samples. HMX from the 10^{16} run was tested with three solvents of different types, as we were somewhat concerned that the results might be affected by reaction of the gases with the solvent.

Table IV

Crystal or Particle Densities of Irradiated Explosives

Explosive	Ref. Values	Measured Density (g./cc.)			
		Control	Irradiated		
			$10^{16}(-80^{\circ}\text{F})$	$10^{15}(+100^{\circ}\text{F})$	$10^{15}(-80^{\circ}\text{F})$
RDX	1.80	1.81	1.49	1.78	1.80
HMX	1.90	1.87	1.53		
PETN	1.77	1.73	1.42	1.76	1.71
Tetryl	1.73	1.72	1.69		1.73
TNT	1.65	1.65	1.64	1.65	
Comp. B		1.74	1.52		
9010		1.66	1.43		
9404		1.73	1.59		
9407		1.76	1.57		

Table V

Volume and Composition of Evolved Gases,^a 10¹⁵ Run

Sample		Volume (μ l./g., STP)	COMPOSITION (mole percent)							
			$H_2(CH_4)$	N_2	N_2O	NO	CO	CO_2	HCHO	H_2O
TNT	-80°F	3.50	5.1	negl.	10.3	4.6	30.6	36.9	negl.	11.4
TNT	+100°F	10.6	5.3	negl.	16.9	2.3	24.8	45.0	negl.	5.0
HCX	-80°F	21.2	19.7	32.6	7.5	6.5	6.7	5.7	0.4	0.4
9404	-80°F	71.2	7.8	19.5	8.85	9.3	13.0	29.2	0.5	5.1
9404	+100°F	98.5	5.6	25.9	7.0	14.4	13.4	25.4	0.4	4.6
RDX	-80°F	101.	4.6	52.2	9.5	2.6	3.1	25.4	0.1	2.0
RDX	+100°F	240.	3.0	46.6	12.4	1.8	3.6	26.9	0.3	4.4
Comp. B	-80°F	122.	3.9	49.3	8.5	2.3	5.4	23.7	0.1	2.7
Comp. B	+100°F	203.	2.3	46.0	8.9	2.0	5.0	26.2	0.3	7.1
NC	-80°F	135.	8.4(3.3)	7.2	11.0	6.0	32.8	30.2	0.1	1.1
NC	+100°F	178.	5.4(4.2)	8.8	13.2	7.4	29.6	29.1	0.2	2.2
9010	-80°F	125.	5.1	28.3	20.3	2.6	9.0	33.5	---	0.8
9010	+100°F	216.	4.5	30.9	20.8	1.1	7.0	34.4	---	0.8
PETN	-80°F	258.	6.2	28.6	2.6	22.4	16.8	5.5	---	5.2
PETN	+100°F	308.	4.3	33.3	3.0	20.9	19.2	6.2	---	9.1
9407	-80°F	244.	2.6	43.9	12.9	0.7	7.5	24.7	trace	6.7
9407	+100°F	354.	2.0	49.1	11.9	1.1	7.6	26.5	trace	1.4

^aAfter correction for residual air. See text.

Table VI

Volume and Composition of Evolved Gases,^a 10¹⁶ Run

Sample	Volume (cc./g., STP)	COMPOSITION (mole percent)							
		H ₂	N ₂	N ₂ O	NO	CO	CO ₂	HCHO	H ₂ O
TNT	0.75	4.25	21.43	7.76	0.61	13.61	50.94	--	0.76
Tetryl	8.20	0.72	42.49	3.38	1.66	9.97	41.50	0.06	--
NC	36.0	0.83	34.15	13.71	11.18	5.73	34.38	--	--
Comp. B	42.9	0.19	54.97	12.43	0.22	4.45	27.37	--	--
9010	59.7	0.27	57.30	10.04	0.24	2.48	29.64	0.01	--
RDX	68.6	0.19	54.80	13.45	0.24	2.74	28.54	0.03	--
9407	70.8	0.30	59.58	9.41	0.62	1.97	28.10	--	--
PETN	71.7	0.53	22.55	18.97	--	4.74	53.04	--	--

^a The data in this table do not account for all the volatile products evolved by the samples. See text.

Table VII

Volume and Composition of Trapped Gases, 10^{16} Run

Sample	Solvent ^a	Total Volume (cc./g.)	Composition (mole percent)					
			N ₂	N ₂ O	NO	CO	CO ₂	H ₂ CO
HMX	γ -BL	8.8	83.8	3.8	0.2	5.0	6.8	0.4
HMX	CH	8.9	80.9	6.8	0.4	0.8	10.9	0.1
HMX	DMF	7.4	75.1	8.0	0.1	2.3	14.4	0.1
HMX (10^{15} +100°F)	γ -BL	0.3	73.5	10.7	1.7	---	14.1	---
HMX (Control)	γ -BL	0.0						
RDX	γ -BL	3.7	78.1	9.2	0.5	0.4	10.9	0.9
PETN	γ -BL	2.3	29.2	14.4	2.6	4.4	49.4	---
Tetryl	γ -BL	< .01	67.4	?	?	?	32.6	---
NC	γ -BL	< .01	Mostly air				trace	
9010	γ -BL	2.7	76.5	10.5	0.3	2.0	10.6	trace

^a Solvents: γ -BL = γ -Butyrolactone, CH = Cyclohexanone, DMF = Dimethylformamide

There is some indication that this may have been the case with dimethylformamide, although the reproducibility of these measurements is probably not too good, primarily because of the sampling problem. In any event, as a result of the tests made with HMX, and also because it is a reasonably good solvent for these materials, γ -butyrolactone was used for the remainder of the measurements.

X-Ray Diffraction and Microscopic Examination. - X-ray powder patterns were obtained on the control and 10^{16} irradiated samples of all the one-component explosives. The pattern for NC changed completely, with the single prominent line in the control sample being entirely absent in the irradiated sample. There appeared to be a slight amount of line broadening in the RDX pattern, and possibly in the HMX and PETN patterns. No change could be detected in the TNT or tetryl patterns.

Microscopic examinations of the 10^{15} samples revealed only minor changes in color or opacity of the crystals. In the case of the 10^{16} samples, the most prominent changes (aside from color changes in the aromatic compounds) were the changes in transparency of the crystals, particularly in the case of RDX, HMX, and PETN. The original crystals were clear except for gross imperfections, while the irradiated crystals were white and opaque. Numerous small voids could be seen in the crystals of these materials, and also, to a lesser extent, in the TNT and tetryl samples. The crystallization rates of the last two materials, after melting, also appeared to be much lower than those of the corresponding control samples.

The NC sample appeared almost unchanged under the microscope except that its color had become slightly yellow. On the other hand, the control sample was readily soluble in acetone, while the irradiated sample was almost completely insoluble.

IR Spectra. - IR spectra were run on the 10^{16} samples. The IR spectra of PETN and NC showed distinct changes after irradiation, consisting of increased OH-stretching absorption and new bands in the carbonyl region (5.75μ). The changes in the spectra of the other materials were minor, suggesting that the color changes which occurred in some of the samples involved only very small fractions of the sample.

Melting Points and Elemental Analyses. - These data are summarized in Tables VIII and IX.

Pyrolysis and DTA Curves. - It isn't possible to reproduce all the curves here on a useful scale, so only the curves obtained for HMX are given (Fig. 1). The principal features of these and the remaining curves are presented and discussed below.

Paper Chromatography. - These results also are presented below.

Drop-Weight Impact Sensitivity. - These results are given in Table X and are interpreted below.

TABLE VIIIMelting Points(°C)

Explosive	m.p.(lit.)	m.p.(control)	m.p.(10 ¹⁶ nvt)	ΔT
TNT	81.1	81-82	78-80	3
Tetryl	131-132	131-132	125-129	6
PETN	140-141	142.5 - 144	131.5 - 138.5	11
RDX	204.5-205	191(decompn.)	191(decompn.)	0
HMX	278	253(decompn.)	244(decompn.)	9

TABLE IXElemental Analyses

		C	H	N
PETN:	Calculated	19.00	2.55	17.73
	Control			17.47
	Irradiated	19.90	2.86	16.62
NC:	Control			11.87
	Irradiated			9.29
RDX:	Calculated	16.22	2.72	37.84
	Control	16.43	3.06	37.27
	Irradiated	16.73	2.95	36.80
HMX:	Calculated	16.22	2.72	37.84
	Control	16.61	2.88	37.52
	Irradiated	17.03	3.20	36.85
Tetryl:	Calculated	29.28	1.76	24.39
	Irradiated	29.92	1.98	23.86
TNT:	Calculated	37.02	2.22	18.50
	Irradiated	37.22	2.41	17.92

Table X

Type 12 Impact Tests, Irradiated Samples

Explosive	Control			Irradiated 10^{15} nvt - 80°F			Irradiated 10^{15} nvt + 100°F			Irradiated 10^{16} nvt - 80°F		
	h(cm.)	m(log)	σ (log)	h(cm.)	m(log)	σ (log)	h(cm.)	m(log)	σ (log)	h(cm.)	m(log)	σ (log)
PETN	13.0	1.1134	0.040	13.2	1.1218	0.026	13.3	1.1256	0.053	13.8	1.1385	0.041
RDX	22.8	1.3579	0.044	22.0	1.3426	0.045	21.4	1.3301	0.029	29.4	1.4676	0.031
HMX	27.4	1.4384	0.041	26.2	1.4176	0.031	25.7	1.4093	0.036	28.8	1.4593	0.036
Tetryl	39.1	1.5926	0.058	43.9	1.6426	0.019	39.1	1.5926	0.045	37.3	1.5718	0.026
NC	64.5	1.8093	0.034	67.6	1.8301	0.043	75.2	1.8760	0.049	No Expl. at 320 cm.		
TNT	150	2.1760	0.029	166	2.2210	0.059	144	2.1593	0.020	160	2.2051	0.013
Comp. B	57.5	1.7593	0.047	59.1	1.7718	0.068	56.4	1.7510	0.020	64.5	1.8093	0.036
9407	35.1	1.5454	0.032	36.2	1.5593	0.049	35.2	1.5468	0.017	40.3	1.6051	0.050
9010	36.7	1.5648	0.023	36.9	1.5676	0.031	34.6	1.5385	0.041	47.4	1.6755	0.036
9404	43.2	1.6357	0.036	42.3	1.6260	0.036	40.3	1.6051	0.013	45.2	1.6551	0.013

Additional comments and observations on the effects of the radiation (primarily the 10^{16} run) on the individual materials are given in the following paragraphs.

HMX. - On the basis of the weight loss measurements, almost ten percent of the sample was lost in the form of volatile decomposition products. The melting point of the irradiated sample is lower than that of the control, and its N content also is somewhat lower. Neither X-ray diffraction, the IR spectrum, nor paper chromatography could detect significant amounts of impurities in the solid residue, but a specific chemical analysis for formaldehyde revealed the presence of 1.0% polyoxymethylenes.

In the solution experiments, approximately 9 ml. of gas was evolved per gram of sample, and this was predominantly N_2 . In the pyrolysis apparatus, gas begins to appear as soon as the temperature starts to rise (see Fig. 1). Slug samples of the gas from the pyrolysis cell were taken at various temperatures and analyzed by gas chromatography. It was found that water vapor was the principal constituent of these at all temperatures below the transition temperature. The trapped gases, and formaldehyde formed by the vaporization and depolymerization of the polyoxymethylenes, accounted for the remainder.

The β - δ polymorphic transition⁹ begins at about 180°C and is accompanied

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⁹ W. C. McCrone, Anal. Chem. 22, 1225 (1950). In this reference the β polymorph is referred to as HMX I, the δ polymorph as HMX IV.

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by the release of another burst of gas. The subsequent thermal decomposition of the sample appears to have been displaced to slightly lower temperatures in comparison with the control sample.

The DTA curve exhibits an exotherm beginning at 50-75°C and peaking at about 155°C. We are unable to propose any chemical reaction, involving the products known to be present, to explain this exotherm and have tentatively concluded that it results from the annealing out of stored energy. The area under the exotherm is several times the area of the endotherm corresponding to the β - δ transition in the control sample. The energy of this transition has been measured¹⁰ and amounts to about

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¹⁰ A. T. Blomquist, OSRD Report No. 1227 (unclassified).

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10 cal./g. (at room temperature), so that we obtain 30 cal./g. as a rough estimate of the energy released in the low temperature exotherm. If this is indeed stored energy, we would expect it to be released fairly rapidly under the conditions of the drop-weight impact test, and it is somewhat surprising that the irradiated sample is no more sensitive than the control.

RDX. - The RDX sample was decomposed to the extent of about 16%. The capillary melting point was unchanged, although small changes in the elemental composition were noted, and 0.53% polyoxymethylene was found in the residue by analysis. Here again, however, no significant change in the composition or purity (in particular, in the RDX/HMX ratio) could be detected from the X-ray powder pattern, the IR spectrum, or the paper chromatogram.

The DTA curve for RDX also exhibits an exotherm beginning in the 50-75°C range and peaking at around 160°C. The amount of gas evolved during this process, as determined from the pyrolysis curve, is considerably less than was observed with HMX, and also is less than would be expected from the results of the solution experiments (3.7 ml./g.) and the polyoxymethylene content. However, the RDX exotherm merges into the melting endotherm, and at this point extensive thermal decomposition of the sample begins, with the evolution of considerable gas from this source.

The irradiated sample of RDX is, if anything, slightly less sensitive than the control sample.

PETN. - This explosive lost about 14% by weight in the form of volatile decomposition products, and 92% of the weight loss is accounted for by the volume and composition of the evolved gases. Unlike RDX and HMX, CO_2 was the principal constituent of these, and this is also true of the gases evolved on solution of the crystals.

Elemental analyses, melting point, IR spectrum, and paper chromatography all revealed changes in the composition of the sample. Pentaerythritol trinitrate was detected by paper chromatography, and evidence of the presence of the dinitrate also was obtained in this test. A strong spot test for NO_2 and/or NO_2^- was obtained on the irradiated sample.

The DTA and pyrolysis curves for PETN are quite different from those of RDX and HMX. There is some evidence of a slight exotherm centered around 100°C, and this is accompanied by relatively little gas evolution. The melting endotherm, in agreement with the capillary melting point results,

was shifted to a lower temperature by some 10-15°, and is much smaller in area than that of pure PETN. This may indicate that "annealing" is occurring during melting, or that exothermic chemical reactions are taking place.

In spite of these many changes in the chemical and physical properties of the sample, its impact sensitivity remained essentially unchanged.

NC. - Although nitrocellulose did not initially evolve as much gas, or lose as much weight, as the materials already discussed, the eventual effects of the irradiation were most striking in the case of this material. As already noted, decomposition of the sample continued at a rapid rate after irradiation, and, for all practical purposes, the sample has deteriorated completely. It no longer explodes in the drop-weight test, and also it is the only sample of NC we have tested thus far which failed to "pop" in the DTA apparatus.

The poor agreement between the weight losses determined from the gas analysis data and by direct measurement (see below) indicates that a considerable fraction of the decomposition products were initially present as volatile liquids. In this case, nitric and nitrous acid may have been among these, as a strong test for NO_2 and/or NO_2^- was obtained on the residue.

The pyrolysis and DTA curves for the irradiated sample indicate that a significant exothermic decomposition occurs with a peak at around 110°C. The products evolved in this decomposition (which is not observed in the control sample) were gas chromatographed and found to be oxides of nitrogen and water.

Tetryl. - The weight loss amounted to 1.3% and was all accounted for by the gas analysis data. Very little gas was evolved by the crystals on solution. The DTA curves indicate that melting of the irradiated sample began at a temperature some 15° lower than the control sample, although the capillary melting points differ by only 6°. The pyrolysis curve shows a small amount of gas evolution at the melting point. Otherwise, the curves for the irradiated and control samples are quite similar. Elemental analyses indicated slight changes in composition. These did not show up in the IR spectrum, but paper chromatography indicated the presence of an impurity identified only as a metadinitro aromatic compound.

TNT. - Although the color of the TNT sample changed considerably, all other tests indicated that it was affected only to a minor degree. Elemental analyses indicated some change in composition, and the paper chromatogram revealed the presence of the same metadinitro aromatic compound as was found in the tetryl sample. No change was found in the X-ray powder pattern or IR spectrum, but the capillary melting point of the irradiated sample was 3° lower than that of the control. The DTA curve indicates a still larger change in the onset of melting (about 7°), and also small amounts of gas appeared in the pyrolysis apparatus during the heating and melting of the sample.

The sample lost only 3 mg. of weight per gram of sample, and the change in crystal density is probably within the reproducibility of the flotation method.

Mixtures. - These were affected pretty much as might have been predicted from their compositions and from the results already given for the individual explosive components. From the practical point of view, the data of Tables III and X are of special interest. The large changes in the densities of the consolidated pellets imply a serious degradation in the explosive performance of these four materials. The changes in impact sensitivity are all in the direction of a decrease in sensitivity, although the change is trivial in the case of 9404. Presumably this change in sensitivity is the result of a preferential loss of the more sensitive component of the mixtures (RDX or HMX).

DISCUSSION

General Comments. - For our present purposes, at least, none of the explosives tested suffered significant radiation damage in the 10^{15} run, and TNT was not seriously affected even in the 10^{16} run. On the other hand, it is clear that extensive damage to the aliphatic and heterocyclic compounds occurred at the higher exposure level. Tetryl was affected to an intermediate degree, in accord with its partially aromatic structure. A similar ordering of these materials with respect to resistance to radiation was reported by Kaufman⁴ on the basis of a study of the rate of gas evolution during (and after) irradiation of various explosives with 0.41 Mev. γ rays.

The remainder of our comments will be concerned primarily with the results of the 10^{16} run.

Except for NC, whose structure appears to have been entirely disrupted, the X-ray powder patterns reveal little or no change in the lattices of the irradiated explosives. Most of the gaseous decomposition products escape from the crystal, and the remainder are trapped in internal voids which are large compared to molecular dimensions. The gas pressures in these voids may be quite high. In the case of HMX, for example, the crystal density and volume of trapped gas of the irradiated sample imply an internal pressure of about 1100 psi. It is particularly pertinent to note in this connection that somewhat different results might have been obtained had it been possible to examine the samples promptly after the irradiation. The irradiated HMX crystals are obviously under considerable strain and can be observed to "pop" even on gentle warming. It thus appears likely that the gradual escape of some of the trapped gas, through diffusion or fracture of the crystals, at least in part explains the observation reported by Kaufman that irradiated explosives continue to evolve gas long after the irradiation has been stopped.

A comparison of the data of Tables II and VI indicates that the directly measured weight losses of the samples are not, in general, satisfactorily accounted for by the gas analysis data. This is shown in Table XI, where the weight losses derived from the two sets of data are compared. Agreement to within a few milligrams would be expected if all the volatile decomposition products had been accounted for in the gas analyses.

An explanation for this discrepancy, which is consistent with the available evidence and with our method of handling the samples, is that,

Table XI
Weight Losses by Direct Measurement
and From Gas Analysis Data - 10¹⁶ Run

<u>Explosive</u>	<u>Weight Loss, mg./g.</u>		
	<u>Direct</u>	<u>Gas Anal</u>	<u>Diff.</u>
TNT	3	1	2
Tetryl	13	13	0
NC	90	57	33
Comp. B	78	66	12
9010	118	90	28
RDX	143	106	37
9407	134	107	27
PETN	138	127	11

at the time the tubes were opened on the vacuum line, some of the decomposition products, such as water, formaldehyde, and nitric acid, were present primarily in the condensed phase. They thus did not enter the vacuum line through the break-off seal in detectable amounts, but did subsequently evaporate in varying degrees after the necks of the tubes were broken off prior to determining the weights of the residues.

As an example, we estimate (see below) that 2.7×10^{-3} moles of water was formed during the decomposition of the RDX sample. The free volume of the quartz ampoule, about 20 ml., would provide for only about 1% of this as the vapor, and the concentration of water vapor in the gases over the sample would amount only to about 0.3 mole percent.

On the basis of this explanation it is possible, in the case of the RDX and Composition B samples, to account for the missing products with considerable confidence and thus to achieve a satisfactory material balance. The reason for this is that our past experience on the thermal decomposition of RDX, and our present data on its decomposition by nuclear radiation, indicate that, once the RDX molecule begins to break up, it is converted in its entirety to relatively simple and, for the most part, volatile products; except for the possible presence of some formaldehyde polymer (polyoxymethylenes), the solid residue at any stage remains essentially chemically unchanged starting material. If, therefore, we make the reasonable assumption that our gas analysis data (Tables VI and VII) account for all the N, we can first determine how much RDX was decomposed and thus what is missing in the way of C, H, and O. Proceeding in this

manner we find, from the data given for RDX, that, for each molecule of RDX decomposed, we are missing 5.98 H atoms, 2.90 O atoms, and 1.68 C atoms. In terms of water and formaldehyde, this corresponds to 1.68 molecules of H_2CO and 1.22 molecules of H_2O , with 0.18 atoms of H left over and unaccounted for. The material balance finally obtained in this way for the RDX sample is given in Table XII. Essentially identical results were obtained for the Composition B sample after making small adjustments in the gas analysis data for residual air and the TNT decomposition.

Table XII

Material Balance for RDX - 10^{16} Run

Basis: 1 Mole RDX (222.1 g.)

<u>Product</u>	<u>Moles</u>
RDX	0.836
H_2	0.016
H_2O	0.200
H_2CO	0.276
N_2	0.397
N_2O	0.094
NO	0.002
CO	0.019
CO_2	0.197

It should be noted that the gases evolved by the samples remained in the radiation field for the duration of the exposure, and the data of Tables V, VI, VII, and XII are, therefore, related in some unknown way to the mixture of decomposition products formed initially. The latter also may depend on the total dose as a result of an accumulation of decomposition products (impurities) in the solid residue.¹¹ The differences

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¹¹ A. J. Swallow, "Radiation Chemistry of Organic Compounds," Pergamon Press, Inc., New York, N. Y., p 33.

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in the compositions given in Tables V and VI are in general nontrivial and in some cases (e.g., PETN) are remarkable. The gas compositions determined for the RDX samples show relatively little variation. N₂ and CO₂ comprise the bulk of these, even at the lower exposure level. In the absence of other gases, at least, a CO₂/N₂ mixture is relatively quite resistant to nuclear radiation,¹² but the situation may change drastically

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¹² P. Harteck and S. Dondes, Second Int. Conf. on the Peaceful Uses of Atomic Energy, P/1769.

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in the presence of oxides of nitrogen.¹³

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¹³ P. Harteck and S. Dondes, Z. physik. Chem. (Frankfurt), 15, 103 (1958).

G-Values. - As already noted, the solid residue which remains after the irradiation of RDX (or HMX) is predominantly chemically unchanged starting material. The weight loss measurements can, therefore, be used to compute G-values (number of molecules destroyed/100 e.v. of absorbed energy) for these materials. Under the conditions of our experiments, energy absorption occurs primarily through the absorption (Compton scattering) of γ rays and the elastic scattering of fast neutrons. Upper limits for the contributions from the $H(n,\gamma)D$ and $N^{14}(n,p)C^{14}$ reactions also were estimated, however, as these reactions have sizeable cross sections for thermal neutrons. The results of the energy absorption calculations for the 10^{16} run may be summarized as follows:

<u>Source</u>	<u>Energy Deposited</u> <u>(10^{21} e.v./g. of sample)</u>
γ absorption	13.5
Fast neutrons scattering	
by protons	1.3
by C, N, and O	0.6
$N^{14}(n,p)C^{14}$	< 0.07
$H(n,\gamma)D$	< 0.001
Total	15.5

We thus see that γ absorption accounts for almost 90% of the energy deposited in the sample.

After correcting the weight loss data for the polyoxymethylene content of the residues, we find that RDX and HMX were decomposed to the extent of 16.4% and 11.0%, respectively. Combining these figures

with the figure given above for energy deposition, we obtain G-values of 2.9 and 1.4 for the decomposition of RDX and HMX, respectively.

Although these values may be in error by as much as 40% (primarily because of uncertainties in the dosimetry data), they do not appear to be excessively high, and, in particular, they do not suggest that the ability of these compounds to decompose with the evolution of considerable chemical energy augments significantly the primary damage producing process through the agency of some sort of thermal chain.

The decomposition reactions of the other compounds studied are complex, with the residues being mixtures of starting material and solid decomposition products. Hence G-values could not be derived from the weight loss measurements in these cases. Also, the weight losses in the 10^{15} run were not determined with sufficient accuracy to justify the calculation of G-values.

GODIVA TEST

The question of whether a very high dose rate might have unexpected effects on an explosive was briefly investigated using the Los Alamos critical assembly known as Godiva II.¹⁴ The explosives included in this

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¹⁴ T. F. Winett, R. H. White, W. R. Stratton, and D. P. Wood, Nuc. Sci. and Eng. 8, 691 (1960).

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test were TNT, HMX, 9010, 9404, and a 75/25 - RDX/TNT mixture known as Cyclotol. The samples were sealed in quartz containers, as before, and exposed to a single Godiva radiation burst.

At the location of the samples, the total dose delivered by the Godiva pulse is quite small, about 7×10^{12} n/cm.². However, the width of the pulse at half-height is only about 90 μ sec., so that the peak flux is high -- estimated at 10^{17} n/cm.²/sec. The γ dose is small (about 1200 r.) because of self-shielding.

Examination of the samples after this exposure revealed negligible damage, and, in particular, none of the samples exploded.

CONCLUDING REMARKS

The above results indicate that organic explosives do not exhibit unusual behavior, in comparison with other organic compounds, when subjected to moderately high doses of nuclear radiation. This statement must immediately be qualified, however, by noting that the comparison necessarily is made with systems which are, at best, only remotely related to those studied by us. There also do not appear to be any unusual hazards associated with irradiated organic explosives with the exception of nitrocellulose, whose rapid post-irradiation decomposition would probably lead to ignition in a greater bulk of this material. This statement also is subject to one possibly important qualification involving the as yet unexplained low temperature exotherms observed in the DTA curves of some of the samples, most notably in that of HMX. Although this "stored energy", chemical or otherwise, does not affect the impact sensitivities of the samples, its sudden release under other circumstances could possibly be troublesome if our somewhat crude estimates of its magnitude are anywhere

near correct. These exotherms merit further study, and it is unfortunate that insufficient sample remained from our experiments to permit us to pursue the matter.

It is, of course, well known that large quantities of energy (hundreds of calories per gram) can be stored in irradiated graphite in the form of lattice defects, but we are not aware of any quantitative measurements of this sort on crystalline organic compounds such as we are concerned with here. It is also well known that significant concentrations of free radicals can be stored for extended periods of time in irradiated polymers and other organic compounds. While in this case the free radicals themselves represent only quite small amounts of stored energy, they can, in favorable cases, initiate exothermic reactions in the matrix material. It does not appear likely that this could occur in HMX, since nitro groups are notorious chain terminators. Finally, we cannot exclude the possibility that these exotherms result from some exothermic reaction of a more ordinary sort involving the decomposition products trapped in the residue. However, in the case of the HMX sample, at least, the residue contained only a percent or two of what would appear to be fairly innocuous impurities.

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J. A. Sayeg of Group H-4 (IASL) provided and counted the IASL dosimeters used in the tests, and our colleagues in Group GMX-2 (IASL), R. N. Rogers, R. F. Warner, D. L. Upham, H. H. Cady, H. E. Ungnade, and S. K. Yasuda, contributed generously with engineering support, experimental data, and helpful discussions.

Fig. 1. - DTA (upper) and pyrolysis curves for control and irradiated (10^{16} run) HMX samples. The scale at the left is for the DTA curves. The vertical scale for the pyrolysis curves is arbitrary.

DTA Sample—Reference