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NAVORD REPORT

4296

STATION OF NORMAL PROPYL NITRATE BY COMPRESSION OF AIR - NORMAL
PROPYL NITRATE VAPOR MIXTURES

FC

17 MAY 1956



U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

U. S. NAVAL ORDNANCE LABORATORY

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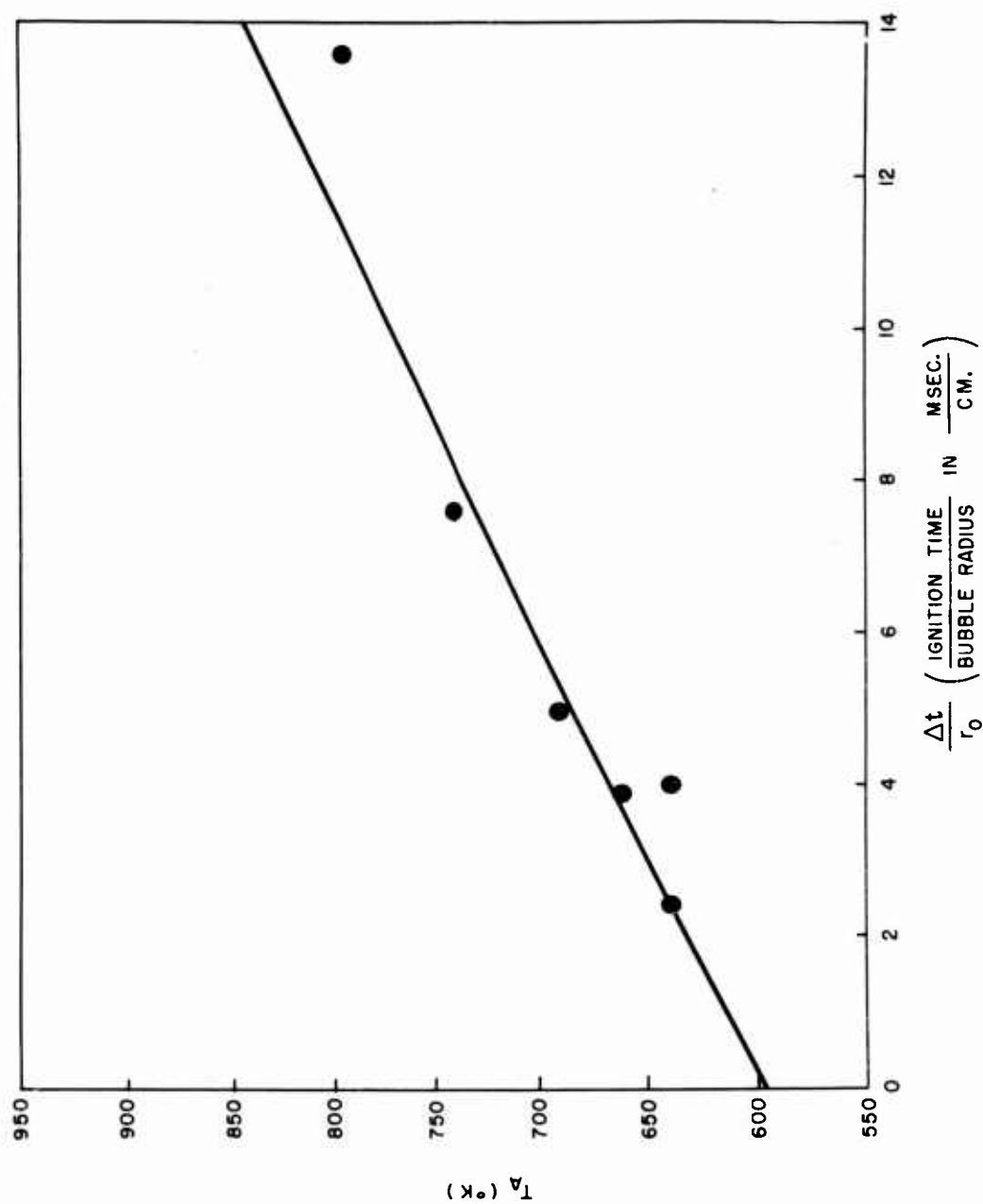


FIG. 1 THE EFFECT OF BUBBLE SIZE AND COMPRESSION TIME ON THE
IGNITION OF n-PROPYL NITRATE

IGNITION OF NORMAL PROPYL NITRATE BY COMPRESSION
OF AIR-NORMAL PROPYL NITRATE VAPOR MIXTURES

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ABSTRACT: The ignition of liquid n-propyl nitrate by the rapid compression of entrapped air bubbles has been studied in a locked-stroke compressor. A minimum bubble size for ignition under the particular conditions has been observed and ease of ignition has been found to increase with increasing bubble size. The results have been analyzed in an approximate fashion.

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NAVORD Report 4296

17 May 1956

The research reported herein was carried out under Task Assignment U1-6-253-12. Data has been obtained on the effect of bubble size on the ignitability of air-normal propyl nitrate vapor mixtures under rapid compression. This work was directed toward an understanding of the factors affecting the safe handling of normal propyl nitrate.

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IGNITION OF NORMAL PROPYL NITRATE BY COMPRESSION
OF AIR-NORMAL PROPYL NITRATE VAPOR MIXTURES

INTRODUCTION

As part of the program to study the hazards associated with the use of normal propyl nitrate (NPN) a study of the rapid compression of air-NPN vapor mixtures above liquid NPN was begun and the results obtained are reported here.

EXPERIMENTAL

The study was carried out in the locked-stroke compressor described in References (1), (2) and (3). In this compressor, a volume of gas is rapidly compressed by a piston driven by a larger piston under a predetermined initial pressure. At the end of the stroke the piston is locked in place, thus maintaining essentially constant volume, and hence constant pressure except for pressure drop due to cooling by the walls.

The pressure-time trace is recorded on an oscilloscope and the trace is photographed by means of a drum camera. Light emission is detected by a photomultiplier tube which "looks" through the window and shows up as a brightening of the pressure trace. The time at which light is emitted can thus be found.

For each experiment a U-tube closed at one end and containing liquid NPN was introduced into the working chamber of the compressor. An air bubble of controlled size was contained in the closed end of the U-tube. A layer of water was placed over the NPN in the open end of the U-tube. This was to prevent possible ignition of the NPN by the compressed helium used in the chamber.

The inside diameter of glass tubing used was 0.33-0.34 cm. The closure was formed by a square-cut piece of glass rod sealed into the end with a minimum of distortion; the length of the bubble was measured by a vernier caliper from the end of the glass rod to the bottom of the liquid meniscus.

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A driving pressure of 180 psia was used on the large piston of the apparatus. A compression ratio of about 17:1 was obtained using a 0.25 in. spacer between the piston and the end of the chamber. Peak pressures in the range 700-800 psia were obtained, with compression times of 1-4 millisecc.

RESULTS

The results are summarized in Table I. For runs 3-9, light emission was observed and this is interpreted as ignition occurring in the bubble. The U-tube was observed through the window at the end of the run while the chamber was still under pressure. In runs 3-9, there was evidence that some of the liquid has been consumed; this was especially noticeable for runs 7-9. For runs 1 and 2, no light emission or change in bubble volume was noted.

For the compressions during which light was emitted, that with initial volume of 0.056 cc gave a single maximum in light intensity near the peak pressure. Bubbles larger than this showed two maxima in the light intensity. The data obtained from the records were the pressure and time at which each ignition occurred and the peak pressure and total time of compression. These data are recorded in Table I. The pressure corresponding to the first ignition will be referred to hereafter as P_i and the peak pressure as P_f .

DISCUSSION

The points of interest in these results are that (a) ignition occurred in the gas phase but did not propagate through the liquid; (b) in some cases apparently two ignitions were observed; (c) the time interval before the first ignition decreased with increasing bubble size.

Points (a) and (b) suggest that the following occurred: The bubble was compressed until it became hot enough to ignite. The vapor then burned out. In the larger bubbles this occurred at a point fairly early in the compression stroke (in run 8, $P_i = 377$ psia vs $P_f = 736$ psia) so that there was time for more material to evaporate and be ignited. In the smaller bubbles the first ignition occurred close to the peak pressure (run 3, $P_i = 790$ psia vs $P_f = 849$ psia) so that there was time for only one ignition.

The failure of burning to propagate through the liquid may simply be due to the fact that the pressures attained were below the minimum pressure at which burning can be

TABLE I
COMPRESSION OF NPN-AIR ABOVE LIQUID NPN

Initial temp. 25°C, Initial pressure=1 atm.

Run	Initial Length (cm.)	Initial Volume (cc.)	1st light emission pressure (psia) (P_1)	time to 1st light emission (msec.)	2nd light emission pressure (psia)	time to 2nd light emission (msec.)	peak pressure (P_f) psia	time to peak pressure (msec.)
(1)	1.11	0.024	No light observed				693	3.08
(2)	.53	0.045	No light observed				Not measurable	
(3)	.62	0.056	790	3.24			849	3.70
(4)	.73	0.062	575	1.86	696	2.31	765	3.02
(5)	.80	0.077	Trace missed - evidence of propagation from bubble size					
(6)	.92	0.079	427	1.34	504	1.95	765	3.72
(7)	1.32	0.12	319	0.75	480	1.47	681	2.13
(8)	1.58	0.143	315	1.87	389	2.5	805	**
(9)	1.60	0.154	377	1.32	467	1.90	736	4.01

** Time of peak not estimated.

sustained in NPN in these tube diameters. No data is available on the minimum burning pressures for NPN burning in tubes and this aspect deserves study.

Qualitatively the fact that the interval before ignition decreased with the increasing bubble size is really an indication that for the larger bubbles the compressions were more nearly adiabatic. This can be demonstrated and the data treated in the following way. Let the temperature at the instant of ignition for all the cases be T_1 and let T_a be the temperature that would have been reached at the ignition pressure if the process had been adiabatic. The heat that the bubble has lost is

$$q = \frac{4}{3} \pi r_o^3 \rho_o (T_a - T_1) C_v \quad (1)$$

where r_o is the initial radius, the bubble being considered spherical and of constant size, while ρ_o is the initial vapor density in the bubble. Since $\frac{4}{3} \pi r_o^3 \rho_o$ represents the initial mass of the bubble, the above equation ignores evaporation as a factor and is based on heat transfer by conduction alone. This is an assumption of this treatment.

The heat transferred to the liquid may also be expressed by

$$q = 4 \pi r_o^2 h \left(\frac{T_1 - T_o}{2} \right) \Delta t \quad (2)$$

where Δt is the interval before ignition, h is the heat transfer coefficient and T_o is the initial temperature; $\frac{T_1 - T_o}{2}$ is thus an average temperature for the time Δt .

The assumptions implicit in equation (2) are that (a) h is a constant (b) the bubble radius is a constant and is equal to the initial value and (c) the temperature difference between the bubble and the liquid may be adequately be expressed by $1/2(T_1 - T_o)$. To replace these assumptions by exact expressions would be enormously difficult. It seems worthwhile to carry through the approximate treatment bearing its limitations in mind and to see how well the results may be interpreted. Equating (1) and (2) and solving for $T_a - T_1$ results in

$$T_a - T_1 = \frac{3}{2} h \frac{T_1 - T_o}{C_v \rho_o} \frac{\Delta t}{r_o} \quad (3)$$

Since T_i is taken as a constant, equation (3) thus predicts that a plot of T_a vs. $\Delta t/r_o$ should be linear and intercept the ordinate axis at T_i .

For the calculation of T_a it is necessary to know C_v from which $C_p/C_v = \gamma$ can be found. The vapor pressure of NPN at 30° is 32.2 mm (5) so that the bubble composition would be

$$\text{NPN} = \frac{32.2}{760} = .042 \quad \text{Air} = 0.958.$$

The heat capacity, C_v , for air may be calculated (4) as

$$C_v = 4.32 + 8.4 \times 10^{-4} T$$

while that for NPN may, as an approximation be taken as 36.4 cal/degree. (From the data of Gray et al. (6), C_v for ethyl nitrate is 29 cal deg. $^{-1}\text{mole}^{-1}$. The difference between the heat capacities for ethanol and n-propanol (7) is 7.4 cal. deg. $^{-1}\text{mole}^{-1}$. The value for n-propanol (7) is thus taken as $29 + 7.4 = 36.4$ cal deg. $^{-1}\text{mole}^{-1}$.) For the mixture then $C_v = 0.958 (4.32 + 8.4 \times 10^{-4} T) + 0.042 \times 36.4$; at 300°K $C_v = 5.99$ and $\gamma = 1.34$; at 1000°K $C_v = 6.47$ and $\gamma = 1.31$. A mean value of $\gamma = 1.33$ may then be taken and T_a calculated from the ignition pressures by

$$T_a = 298 \times \left(\frac{P_f}{P_o} \right)^{\frac{\gamma-1}{\gamma}}$$

The data are summarized in Table II for the six runs wherein ignition was observed and ignition pressures and times were recorded.

TABLE II
CALCULATED ADIABATIC TEMPERATURE AND COMPRESSION TIMES

Run	V_0	r_0	P_1	T_a	t	$\frac{\Delta t}{r_0}$
	cc	cm	psia	°K	msec	msec/cm
(3)	.056	0.239	790	799	3.24	13.68
(4)	.062	0.245	575	739	1.86	7.60
(6)	.079	0.266	427	688	1.34	5.04
(7)	.120	0.305	319	641	0.75	2.46
(8)	.143	0.322	315	638	1.26	3.90
(9)	.154	0.332	377	667	1.32	4.00

Figure 1 illustrates a plot of T_a vs $\Delta t/r_0$ and the points do fit a straight line. The value of T_1 found from the intercept is 595°K.

The fact that at $\frac{\Delta t}{r_0} = 0$, $T_a = T_1$, shows that for these conditions the compression is truly adiabatic, i.e., the ignition temperature is the same as the calculated adiabatic temperature. There are two cases that fit these conditions, an infinitely large bubble $1/r_0 = 0$, and an infinitely fast compression $\Delta t = 0$. For all real cases, as the graph shows, $T_a > T_1$ and the difference measures the amount of heat lost, or the non-adiabaticity of the process.

The truly adiabatic compression of a bubble is, of course, the most favorable case for ignition. According to the above results the temperature that must be attained by such a compression if ignition is to occur is 595°K. Starting from 300°K this would require a compression of about 13 fold, e.g., from 1 to 13 atmospheres. Since all real compressions are in some measure non-adiabatic, this figure represents the minimum compression ratio necessary for ignition of the bubble. Any factor less than this would not yield ignition regardless of bubble size or compression rate.

This is an important result. The mathematical treatment has been approximate rather than rigorous and further studies are needed to test the conclusions drawn here. Such work is in progress at this Laboratory.

SUMMARY

The ignition of liquid n-propyl nitrate by the rapid compression of entrapped air bubbles has been studied in a locked-stroke compressor. The liquid has been contained in small (3.5 mm i.d.) glass U-tubes. Air bubbles ranging from 0.05 to 0.15 cc in volume have been trapped in the closed end of the U-tube and the system subjected to compression at the rate of about 20,000 atm. per second.

At bubble sizes greater than 0.05 cc ignition as evidenced by light emission has been observed. The time interval before ignition and the pressure at ignition have been found to decrease with increasing bubble size.

Making certain simplifying assumptions the data has been analyzed. From this treatment an ignition temperature of 595°K for NPN-air bubbles has been found, corresponding to a compression ratio of about 13:1 for the ideal, perfectly adiabatic compression. For compressions having a compression ratio less than this, the analysis used predicts that ignition will not occur regardless of bubble size or compression rate.

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REFERENCES

1. NAVORD Report 2840, George J. Bryan, 15 Oct 1953, Confidential.
2. NAVORD Report 3703, George J. Bryan and J. W. Enig, 10 Dec 1954, Confidential.
3. NAVORD Report 3818, George J. Bryan, 20 Oct 1955, Confidential.
4. NDRC Report No. A-116, J. O. Hirschfelder, F. T. McClure, C. F. Curtiss, and D. W. Osborne, "Thermodynamic Properties of Propellants Gases". Nov 22, 1942.
5. Ethyl Corporation Report RM-124, by G. W. Thomson, "Some Properties of Propyl Nitrate", (Air Force Project No. 54-630-428, under Contract AF 33 (616)-2397) Dec 17, 1954.
6. P. Gray. M. W. T. Pratt and M. J. Larkin, J. Chem. Soc., 1956, 290 (1956).
7. G. C. Sinke and T. De Vries, J. Am. Chem. Soc., 75, 1815 (1953).

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