

k = Boltzmann constant, g. cm.²/sec.², ° R.
 m = molecular mass, g.
 y = mole fraction in vapor
 x = mole fraction in liquid
 γ = activity coefficient in liquid
 P = total pressure, p.s.i.a.
 P_1 = partial pressure of component (1) in the vapor, p.s.i.a.
 p^0 = vapor pressure of pure component, p.s.i.a.
 T = absolute temperature, ° R.
 R = gas constant, cal. ° R.⁻¹
 $A = 4\sigma^2 \pi^{1/2} m^{-1/2} k^{-3/2}$
 B = correlation constant, $\ln(N/A)^{1/2}$
 C = correlation constant, $E/2R$
 E = activation energy, cal.

Subscripts

1 = hydrogen peroxide

2 = water
3 = oxygen and nitrogen

LITERATURE CITED

- (1) Black, C., *Ind. Eng. Chem.* **50**, 391, 403, (1958); **51**, 211 (1959).
- (2) Monger, J.M., Baumgartner, H.J., Hood, G.C., and Sanborn, C.E., *J. CHEM. ENG. DATA* **9**, 107 (1964).
- (3) *Ibid.*, **47**, 1040 (1955).
Satterfield, C.N., Kavanagh, G.M., Resnick, Hyman, Mass.
- (4) *Inst. Tech. Rept. No. 53*, June 1, 1958.
- (5) Satterfield, C.N., Kavanagh, G.M., Resnick, Hyman, J. *CHEM. ENG. DATA* **4**, 131 (1959).
- (6) Scatchard, G., Kavanagh, G.M., Ticknor, L.B., *J. Am. Chem. Soc.* **74**, 3715 (1952).
- (7) *Soc.* **74**, 3715 (1952).

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Detonations in Hydrogen Peroxide Vapor

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Experiments have been conducted at 2.90, 6.77, and 14.7 p.s.i.a. in order to obtain information concerning the detonation characteristics of hydrogen peroxide vapor. Within the experimental conditions employed, no detonations were observed at 2.90 and 6.77 p.s.i.a. At atmospheric pressure, detonation with a velocity of 6700 feet per second was observed in vapor with a composition of 35 mole per cent hydrogen peroxide.

A FUNDAMENTAL factor in the safe handling of hydrogen peroxide, especially under some of the more severe conditions encountered in military and space applications, is the vapor phase explosion hazard. Previous investigations have been concerned primarily with ignition phenomena. It was of prime interest to know whether or not the vapor would detonate and to gain information concerning some characteristics of the system inside the ignition limits.

The problem is fraught with experimental hazards and the realization of any meaningful data is a laborious procedure. Most of the trouble is caused by the homogeneous and catalytic heterogeneous decomposition of the vapor which greatly complicates obtaining a shock tube filled with vapor of known uniform composition, temperature, and pressure. Generation of vapor with a dynamic system operated by remote control is essential.

EXPERIMENTAL

The system used for study of the hydrogen peroxide vapor explosion velocities is shown schematically in Figure 1. All of the equipment was cleaned and passivated with caustic, nitric acid, and 90%w. hydrogen peroxide. The feed vessel rested on a scale which was used to determine the feed rate. Liquid hydrogen peroxide flowed

from the feed vessel to a constant level feed reservoir. The flow was controlled by a level controller and motor valve. From the feed reservoir, the peroxide entered a reboiler where part of it was vaporized and part drawn off as a bottoms stream. The stainless steel reboiler was of the thermosyphon type, heated by high pressure (up to 150 p.s.i.) steam. The liquid drawn off as bottoms passed through a cooler and into a receiver. The bottoms receiver was vented to the atmosphere during experiments made at atmospheric pressure. During experiments made at lower pressures this receiver was connected to another separate vacuum pump. A sample of bottoms was taken by diverting the stream to a separate receiver. The bottoms rate was determined by measuring the time over which a sample was collected.

Vapor was separated from the liquid in a cyclone which was an integral part of the reboiler. The vapor then entered a 3-inch diameter, 6-inch long vertical section packed with $\frac{3}{16}$ -inch glass helices supported by stainless steel screens (in later experiments these screens were replaced with aluminum screens). From the packed section, the vapor went directly to the explosion tube. It entered the tube at a right angle to the axis of the tube, which was mounted horizontally. After passing through the length of the tube (7-feet 8-inches from center of inlet to center of outlet),

it left vertically downward, made a right angle turn, and entered the quench chamber. In the quench chamber, the vapor encountered a spray of about 1.5 gal. per min. of cold water from a Spraco 6K nozzle. The inert gas and whatever vapor it carried was drawn off through a throttling valve to a three-stage ejector. The liquid accumulated in the bottom of the quench chamber and was drawn off by a stainless steel 1/2-inch Viking pump and discharged, at atmospheric pressure, to the drain. The pump had a packing gland extension and lantern ring through which water passed continuously. The pump ran at constant speed. The discharge to the drain was controlled by a motor valve actuated by a level controller on the liquid in the bottom of the quench chamber. A bypass valve, actuated by the same level controller, was operated so that it opened when the discharge valve closed and vice versa.

Arranged around the tube were six 250-watt Calrod heaters to minimize heat loss from the tube. These heaters were held away from the surface of the tube by three transite spacers and extended longitudinally the full length of the tube. Aluminum foil wrapper around the outside of the heater bundle, which contained the explosion tube in its center, acted as insulation.

The tube itself was a length of 2-inch Schedule 80 Type 6063-T6 aluminum pipe fitted with a tee and blow-out disk at each end. The inside diameter of the pipe was 1.939 inches, the assembled length was 8 feet blow-out disk to blow-out disk, 7 feet, 8-inches from center of inlet to center of outlet. The tube was provided with ports for sampling, spark electrodes, manometer connections, thermocouples, and pressure transducers. The location of these ports and details concerning them are shown in Figure 2.

The system pressure was kept constant during each experiment by bleeding air downstream of the quench chamber. The amount of air bleed was controlled by a manostat. Peroxide of the necessary composition was fed at a constant rate to the reboiler. The boil-up rate was kept steady and the desired reboiler temperature attained by adjusting the amount of bottoms draw-off. Vapor and bottoms samples were taken after all temperatures had become steady. Vapor samples were taken at two or three points along the tube.

The system was operated so that the outer tube wall temperature was 10° to 20° F. above the vapor temperature for several minutes before sampling was begun (Figure 3). These samples were collected alternately rather than simultaneously. Several samplings were taken by switching from one port to the other to make up the composite sample collected from each location. The sample receivers had been brought to a lower pressure than that in the

tube, cooled with liquid nitrogen, and sealed off from the lower pressure source before sampling. This procedure, minimized fractionation of the samples collected, although, of course, only the condensable material was obtained. The samples were analyzed for hydrogen peroxide by the ceric sulfate method. The results were corrected for the presence of oxygen and nitrogen to give the mole fraction of peroxide in the mixture of gas and vapor existing in the tube.

Three different methods of initiation were employed. One form consisted of a 3500 volt capacitive spark obtained by the discharge of two 28 mfd. condensers across a 1/2-inch gap between two tantalum electrodes (one 3/8-inch in diameter, the other 1/8-inch in diameter with hemispherical ends). Another form of initiation was provided by one-inch firecrackers ignited with a resistance wire. The firecracker was contained in an assembly which fitted into the end of the explosion tube. Some of the results were obtained from spontaneous initiation. Data from this form of initiation were used only if it was definitely established that the initiation took place upstream of the detector which triggered the recording circuit.

The electronic system for measuring the velocities is shown in Figure 4. Four SLM PZ 14 piezo pressure transducers were used to record the passage of a pressure wave. One of these transducers served to trigger simultaneously the sweeps on all of the oscilloscopes. The trigger circuit consisted of a piezo calibrator, a wave form generator and a pulse generator. The other three transducers were connected through piezo calibrator-amplifiers to the oscilloscopes. Two bare Chromel-Alumel thermocouples connected directly to oscilloscopes also recorded the passage of a wave. The velocities were calculated from the time-distance relationship of peaks, recorded photographically.

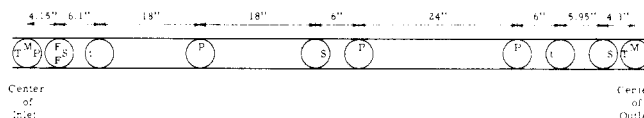


Figure 2. Location of ports in explosion tube

- F. 1/4-inch pipe thread in 3/16-inch thick boss, for firing electrode
 - M. 1/4-inch pipe thread, for manometer connection
 - P. 14 mm. diameter X 1.25 mm. pitch standard spark plug thread, in 5/16-inch thick boss, for pressure transducer
 - S. 1/4-inch pipe thread in 5/16-inch thick boss, for sampling connection
 - I. 3/4-inch pipe thread in 3/16-inch thick boss, for bare thermocouple
 - T. 1/8-inch pipe thread, for thermowell
- (Cross section at each location viewed from inlet, location of symbol indicates circumferential position of port)

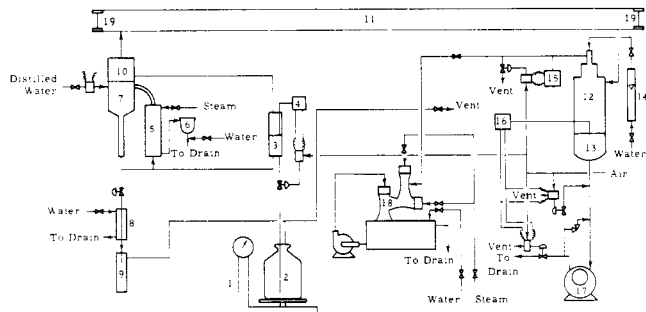


Figure 1. Flow system—explosion tube apparatus

- | | | |
|---------------------|------------------------|----------------------------------|
| 1. Scale | 7. Separator | 13. Liquid surge |
| 2. Feed vessel | 8. Bottoms cooler | 14. Rotameter |
| 3. Feed reservoir | 9. Bottoms receiver | 15. Manostat pressure controller |
| 4. Level controller | 10. Glass de-entrainer | 16. Level controller |
| 5. Reboiler | 11. Explosion tube | 17. Sump pump |
| 6. Steam trap | 12. Quench chamber | 18. Three stage ejector |
| | | 19. Bursting discs |

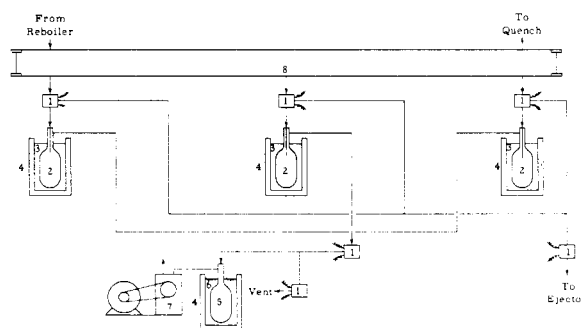


Figure 3. Sampling system for peroxide vapor explosion tube

- | | |
|--------------------|-------------------|
| 1. Solenoid valve | 5. Cold trap |
| 2. Sample receiver | 6. Ice |
| 3. Liquid nitrogen | 7. Vacuum pump |
| 4. Dewar | 8. Explosion tube |

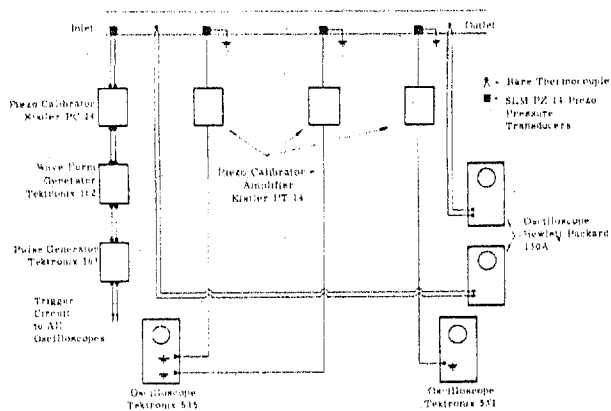


Figure 4. Electronic system for velocity measurements

DISCUSSION

The detonation velocity of hydrogen peroxide vapor was studied experimentally at pressures of 2.90, 6.77, and 14.7 p.s.i.a. The data are shown in Table I and Figures 5, 6, and 7. The range in the values of vapor composition in the tube for a given experiment is indicated along with the average concentration in the figures. The photographs of the oscilloscope traces were carefully analyzed to sort out reflections, spontaneous ignitions between detectors, etc. All ambiguous experiments were discarded. All of the experiments given here showed either steady or increasing velocity of the peroxide decomposition wave. In the case of the data at atmospheric pressure the velocities were sometimes increasing rapidly, and the figure quoted is the velocity in the last third of the tube. The precision in the measurement of velocity between two stations was close to 10%.

Table I. Observed Velocity Data

Press., P.S.I.A.	Av. Vapor Compn. H ₂ O ₂ Mole Fraction	Velocity, Kiloft./Sec.
2.94	0.523	3.1
2.96	0.566	3.3
2.90	0.615	3.3
2.90	0.533	2.9
2.90	0.554	2.8
2.90	0.538	3.3
6.77	0.425	1.7
7.00	0.468	1.7
6.77	0.452	1.6
6.77	0.444	1.6
6.77	0.437	1.9
6.67	0.387	1.9
6.77	0.424	2.4
6.79	0.427	2.5
6.79	0.367	2.0
6.77	0.370	2.5
6.77	0.391	2.4
6.81	0.329	2.0
6.77	0.361	1.9
6.79	0.352	2.2
6.77	0.387	2.3
14.78	0.288	2.3
14.60	0.304	1.5
14.18	0.302	1.8
14.82	0.289	1.4
14.70	0.299	1.4
14.78	0.335	3.6
15.01	0.320	1.5
14.26	0.355	6.7
14.59	0.310	2.5
14.89	0.323	3.9
14.37	0.330	3.1
15.13	0.333	2.5
14.40	0.346	4.8

The acoustic velocity in hydrogen peroxide vapor was calculated with the assumption of an ideal gas from:

$$a = \left(\frac{RRT'}{m} \right)^{1/2} \quad (1)$$

Assuming that only H₂O₂ and H₂O are present in the vapor the average molecular weight is given by

$$m = 18 + 16y = 16(1.125 + y) \quad (2)$$

Thus

$$a = 635.98 \left[\frac{T/100}{1.125 + y} \right]^{1/2} \text{ ft./sec.} \quad (3)$$

The pertinent values of the velocity of sound have been plotted in Figures 5, 6, and 7. Any experimental propagation velocity which does not exceed that of sound is, of course, not a detonation velocity.

In experiments involving initiation by shock, the inlet bursting disk was ruptured. With the system initially at subatmospheric pressure, a steady driven shock wave is established with system pressure on the downstream side

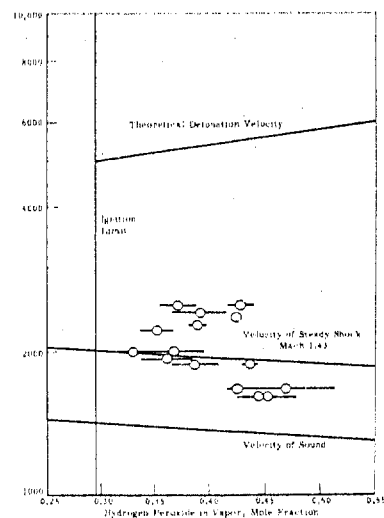


Figure 5. Detonation velocity at 2.90 p.s.i.a.

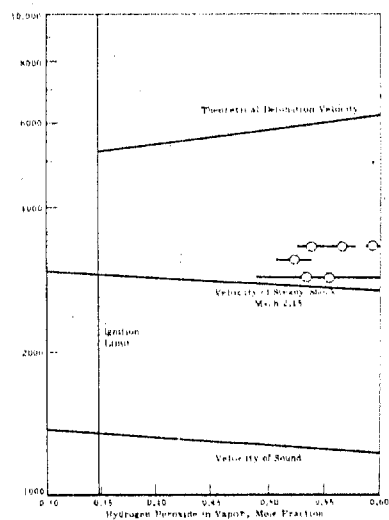


Figure 6. Detonation velocity at 6.77 p.s.i.a.

and atmospheric pressure on the upstream side. The velocity of such a shock can be calculated from

$$M = \left[\frac{r(k+1) + (k-1)}{2K} \right]^{1/2} \quad (4)$$

With $k = 1.3$, the values of M are 1.427 for 6.77 p.s.i.a. and 2.145 for 2.90 p.s.i.a. The velocities corresponding to these steady shock waves are plotted in Figures 5 and 6. For shock initiation at these pressures any experimental propagation velocity which does not exceed that of the driven shock wave is not a detonation velocity.

The theoretical detonation velocity of hydrogen peroxide vapor was calculated from a gas-dynamic approach to explosions in gases leading to the relation (1)

$$M - \frac{1}{M} = \pm \left[\frac{2(k+1)c_p}{c_p T} \right]^{1/2} \quad (5)$$

which can be put in the form

$$M = \left[\frac{q(k+1)}{2c_p T} + 1 \right]^{1/2} \pm \left[\frac{q(k+1)}{2c_p T} \right] \quad (6)$$

where the plus sign corresponds to detonation and the minus sign to deflagration. These equations do not predict whether detonation or deflagration or neither of these will occur but provide a theoretical value of the velocity when they do occur.

The theoretical detonation velocities for the experimental conditions used were calculated and are given in Figures 5, 6, and 7 for comparison with the experimental values.

Also given in the figures are the appropriate ignition limits for the vapor at each pressure (2, 3).

As shown in Figures 5 and 6, at pressures of 2.90 and 6.77

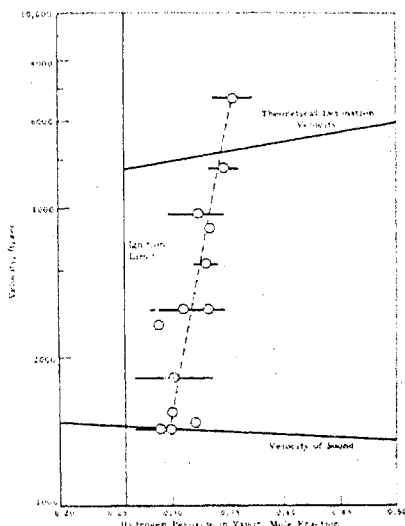


Figure 7. Detonation velocity at atmospheric pressure

p.s.i.a. under the experimental conditions employed, no detonations occurred. With longer, larger diameter tubes and more concentrated vapor, detonation is perhaps possible at these pressures. Such experiments will be difficult because of the necessity for a dynamic system and the progressively increasing difficulty of maintaining a known uniform vapor composition.

The data at atmospheric pressure reveal the existence of detonation. As the vapor composition increased from 0.3 to 0.35 mole fraction peroxide, the reaction velocity increased from that of sound in the medium to 6670 feet per sec. Experiments at higher concentrations were attempted many times with several equipment modifications but were unsuccessful because of spontaneous decomposition or premature ignition of the vapor. The points on the rising portion of the curve in Figure 7 are not necessarily steady state velocities since the velocity over the last interdetector distance was often higher than that over the previous interval. This suggests that the curve in Figure 7 should have a steeper slope. However, detonations with velocities close to theory can be obtained inside the ignition limit of hydrogen peroxide vapor.

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NOMENCLATURE

- a = acoustic velocity (feet/sec.)
- g_c = gravitational constant (32.2 ft. lb. mass/sec.² lb. force)
- k = ratio of specific heats of the unreacted gas
- R = gas constant (1546 ft. lb. force/lb. mole ° R.)
- T = absolute temperature of the unreacted gas (° R.)
- m = average molecular weight (lb. mass/lb. mole)
- y = mole fraction of H₂O₂ in the vapor
- M = Mach number, with respect to the unreacted gas of the detonation (+) or deflagration (-)
- p = pressure ratio across the shock
- q = heat of reaction (B.t.u./lb. mole)
- c_p = specific heat, at constant pressure, of the unreacted gas (B.t.u./lb. mole ° F.)

For hydrogen peroxide vapor:

$$q = 45,450 \text{ B.t.u./lb. mole}$$

$$k = 1.3$$

$$c_p = \left(\frac{k}{k-1} \right) R = \frac{1.3}{0.3} (1.987) = 8.61 \text{ B.t.u./lb. mole ° R.}$$

LITERATURE CITED

- (1) Oppenheim, A.K., private communication.
- (2) Monger, J.M., Baumgartner, H.J., Hood, G.C., Sanborn, C.E., J. CHEM. ENG. DATA 9, 107 (1964).
- (3) Satterfield, C.N., Kavanagh, G.M., Resnick Hyman, *Ind. Eng. Chem.* 43, 2507 (1951).

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