

## DETONATION STUDIES WITH NITRIC OXIDE, NITROUS OXIDE, NITROGEN TETROXIDE, CARBON MONOXIDE, AND ETHYLENE

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### Summary

This paper presents the results of detonation studies conducted by the Bureau of Mines on nitric oxide, nitrous oxide, nitrogen tetroxide, carbon monoxide, and ethylene to evaluate the potential hazards of these materials to explosive shock initiation. Charge arrangements, construction details, and interpretation of results are given.

Nitric oxide was observed to be the simplest known molecule capable of detonation-detonating in all three phases. Nitrous oxide, as a solid, nonboiling liquid, and nitrogen tetroxide and carbon monoxide, as nonboiling liquids, could not be initiated to detonation. Ethylene, as a gas at elevated pressure, gave evidence of a mild reaction but did not detonate; as a nonboiling liquid, it could not be initiated to detonation.

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### Introduction

Damaging explosions propagating in condensed-phase nitric oxide (NO), at the NASA laboratory in Cleveland, Ohio [1], led to the realization that NO was a detonable material. The Bureau of Mines was requested by NASA to investigate and confirm its detonability. Nitric oxide, being exothermic in its decomposition, decomposing to  $N_2$  and  $O_2$ , with an energy release of approximately 3.02 MJ/kg, was of interest to NASA as a means of providing additional enthalpy to a heated air stream to achieve temperatures associated with flows at Mach numbers in the range of 8 to 9. Since storing and pumping liquid NO was preferred to handling the gas phase, it was desirable to characterize the detonability of NO in all three phases. To complement these data, similar investigations were made on nitrous oxide ( $N_2O$ ), nitrogen tetroxide ( $N_2O_4$ ), carbon monoxide (CO), and ethylene ( $C_2H_4$ ). Since liquid carbon monoxide is being transported by truck and its decomposition to C and  $CO_2$  is also exothermic, its detonation hazards are of current interest. The results of these studies are presented in this paper.

## Experimental results and discussion

A variety of containers and initiation sources were used, depending on the properties of the material under study. The instrumented-card gap test [2] was used to study the ease of initiation and extent of propagation in the condensed phase. Simple pressure-activated switches were used to monitor reaction velocities in the gas phase. The materials, obtained as commercial gases, were condensed to the liquid or solid phase as needed by using suitable refrigerants. Measurements were made in the solid, liquid, and gas phases for NO, in the solid and liquid phase for N<sub>2</sub>O, the liquid and gas phase for C<sub>2</sub>H<sub>4</sub>, and in the liquid phase for N<sub>2</sub>O<sub>4</sub> and CO.

### *Gaseous nitric oxide*

Experiments with gaseous NO at ambient temperature were conducted at ambient pressure 0.100 MN/m<sup>2</sup>, and at 2.17, 2.90, and 7.00 MN/m<sup>2</sup>. In several of the earlier tests at ambient pressure, Composition A-5 (98.8% RDX plus 1.2% stearic acid) charges were used as initiators. For the bulk of the experiments, different sized charges of PETN were used to define the charge weight corresponding to the deflagration—detonation threshold at the various initial test pressures. The nitric oxide used in all tests had the following analysis: 97.80% NO, 1.05% N<sub>2</sub>, 1.04% N<sub>2</sub>O, and 0.11% NO<sub>2</sub>.

Experiments at 0.100 MN/m<sup>2</sup> initial pressure were conducted in a closed steel vessel 178 mm in diameter and 3.66 m long. The explosive charge, together with a No. 6 electric blasting cap, was suspended at one end of the vessel, which was then evacuated and filled with NO. Propagation rates were measured at the downstream end of the vessel with pressure-sensitive switches spaced 500 mm apart. The results of the trials at ambient pressure (0.100 MN/m<sup>2</sup>) are presented in Table 1. It will be noted that for initiators weighing  $43 \times 10^{-3}$  kg or less, reaction velocities of the order of 1000 m/s were observed, but velocities in excess of 2000 m/s were observed for initiators weighing  $60 \times 10^{-3}$  kg or more. The high-velocity reactions are almost certainly detonations in the true sense; the lower velocity reactions are presumably unstable and will be referred to as deflagrations.

Initiation studies with gaseous NO were extended to 2.17 MN/m<sup>2</sup> and 2.90 MN/m<sup>2</sup> using 82.6 mm-ID by 1.22-m-long closed steel pipes equipped with the same instrumentation for measuring velocity that was used in the trials at ambient pressure. These results are also presented in Table 1. At 2.17 MN/m<sup>2</sup>, the initiating charge weight corresponding to the deflagration—detonation threshold was between  $2.0 \times 10^{-3}$  and  $20.0 \times 10^{-3}$  kg of PETN; at 2.90 MN/m<sup>2</sup>, the critical charge weight was observed to be between  $1.0 \times 10^{-3}$  and  $2.0 \times 10^{-3}$  kg.

Experiments were extended to higher pressures by allowing measured quantities of liquid NO to vaporize into a closed, high-pressure container at ambient temperature. The arrangement employed for condensing the gas is shown in Fig. 1. The condenser consisted of a 49.25-mm-ID by 5.54-mm-

TABLE 1

Results of gaseous nitric oxide initiation studies at various initial pressures

Initiator weight* ( $10^{-3}$ kg)	Velocity (m/s)	Results
<i>Initial pressure = 0.100 MN/m<sup>2</sup></i>		
10	1000	Deflagration
38	1100	Deflagration
40	1300	Deflagration
43	1100	Deflagration
60	2100	Detonation
84	2300	Detonation
<i>Initial pressure = 2.17 MN/m<sup>2</sup></i>		
0.2	1000	Deflagration
2.0	700	Deflagration
20.0	1900	Detonation
<i>Initial pressure = 2.90 MN/m<sup>2</sup></i>		
0.5	200	Deflagration
1.0	500	Deflagration
2.0	—	Detonation**
3.0	2100	Detonation
<i>Initial pressure = 7.00 MN/m<sup>2</sup></i>		
0.05	300	Deflagration***
0.05	—	No reaction
0.60	500	Deflagration
0.90	2100	Detonation

\* Initiating charges were PETN pressed to a density of  $1.5 \times 10^3$  kg/m<sup>3</sup> except those in italics, which were composition A-5 pressed to a density of  $1.65 \times 10^3$  kg/m<sup>3</sup>. All booster charges were initiated with a No. 6 electric blasting cap except the  $0.05 \times 10^{-3}$  kg PETN charge used at 7.00 MN/m<sup>2</sup>; in this case, the charge was initiated with  $0.075 \times 10^{-3}$  kg of lead azide.

\*\* Velocity instrumentation failed in this firing; result decided on basis of damage to velocity switches.

\*\*\* Initial pressure was 6.31 MN/m<sup>2</sup>.

wall steel pipe 508 mm long immersed in a liquid N<sub>2</sub> bath. After the required amount of NO had been collected, the condenser was warmed with an electric heating element, and the NO gas was transferred at a predetermined pressure to the test container, which consisted of a 914-mm-long, 49.25-mm-ID by 5.54-mm-wall steel pipe. In two experiments with gaseous NO at 7.00 MN/m<sup>2</sup>,  $0.6 \times 10^{-3}$  kg, and  $0.9 \times 10^{-3}$  kg of PETN, induced a deflagration and a detonation, respectively. Smaller initiators, consisting of  $0.050 \times 10^{-3}$  kg PETN and  $0.075 \times 10^{-3}$  kg of lead azide contained in a gelatin capsule and

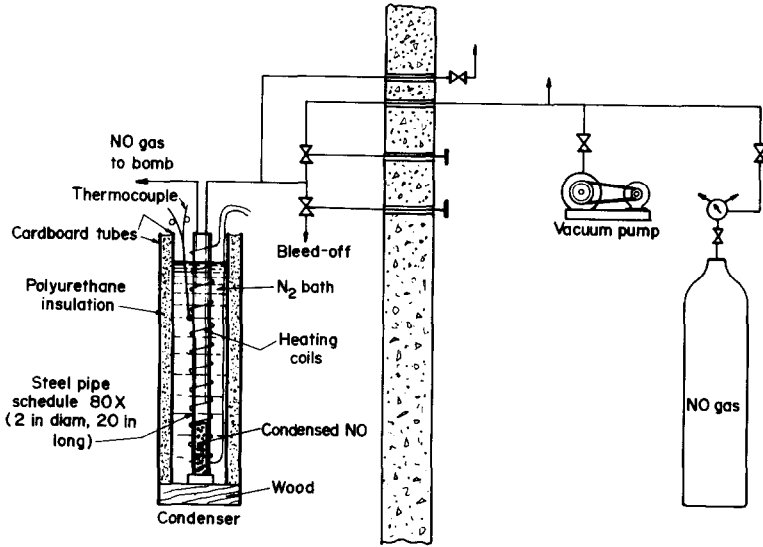


Fig. 1. Arrangement for condensing NO gas.

initiated with a hot bridge wire, induced a deflagration in NO at  $6.31 \text{ MN/m}^2$ . In a similar firing at  $7.00 \text{ MN/m}^2$ , there was no reaction. The results of the tests at higher pressures are also given in Table 1; all of the results with gaseous NO are plotted in Fig. 2, which shows the relationship between the initial pressure and the initiator weight corresponding to the deflagration detonation threshold. Although no attempt was made to measure detonation pressures,

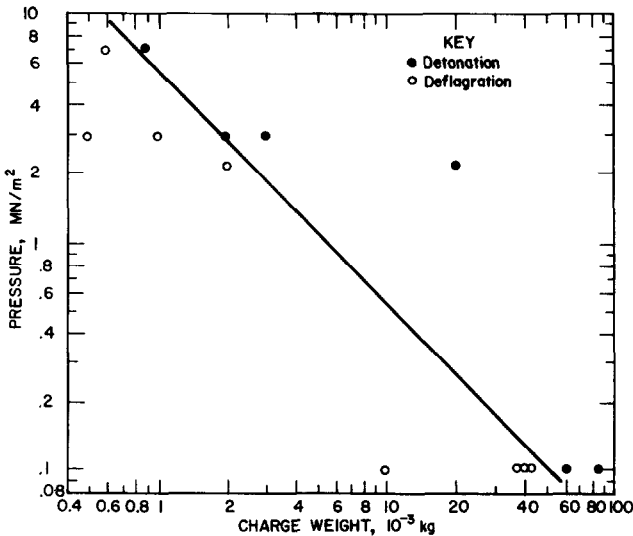


Fig. 2. Effect of initial nitric oxide pressure on charge weight.

equilibrium calculations predict pressure ratios about 21 times the initial pressure for the pressure ranges investigated in this program. From previous work [3], it was observed that for gas deflagrations in a nonventing system, the peak pressures (constant volume explosion pressure) were about one-half the pressure of the same gas mixture when detonated. Thus, from a safety viewpoint, one should be aware of expansion ratios of the order of 10 from a rapid combustion process, which can be initiated with considerably less energy than a detonation. While no attempt was made to define the minimum explosive energy to induce deflagration, some insight has been obtained from the experiments conducted. At ambient pressure, the smallest initiator of  $10 \times 10^{-3}$  kg PETN resulted in deflagration as did a  $0.050 \times 10^{-3}$  kg PETN initiator at  $6.31 \text{ MN/m}^2$ .

The effectiveness of chemical energy initiators can be compared with that of exploding wire initiators when the stored electrical energy is equal to the heat of explosion of the chemical energy sources [4]. PETN has a heat of explosion of about 6.3 MJ/kg. Therefore, to initiate detonation in NO with an electric discharge at ambient pressure would require a stored energy of about 310 kJ, and at  $7.00 \text{ MN/m}^2$ , would require a stored energy of about 4.7 kJ; in either case, a rather substantial energy source. It appears from the limited data available that initiation of deflagrations in the region of  $7.00 \text{ MN/m}^2$  would require about 285 J.

### *Boiling NO*

Liquid NO was prepared in a closed system by first condensing the gas as a solid in a glass vessel immersed in a liquid nitrogen bath. The solid NO was then slowly melted and the liquid poured into a 26.64-mm-ID by 3.38-mm-wall steel pipe, 406 mm long, open to the atmosphere at the top and closed at the bottom with a 0.08-mm thick Teflon\* membrane. The steel pipe, insulated with plastic foam, was precooled with liquid  $\text{N}_2$  to minimize boil-off of the liquid NO.

Experimental results are given in Table 2 (series A) for liquid NO boiling at 121 K and atmospheric pressure. In the first trial, when boosted with a  $50 \times 10^{-3}$  kg tetryl donor, and with only the 0.08-mm Teflon as a gap, boiling NO detonated at high velocity; high-velocity detonations were also obtained with attenuated shocks at 102- and 254-mm gap thicknesses. The average detonation rate of boiling NO was approximately 5400 m/s. Since the observed detonation velocity was very near that of the velocity of sound in the steel container ( $\sim 5000 \text{ m/sec}$ ), care was taken to assure that the velocity probe did not respond to a wave in the container wall generated solely by the explosive initiator. Since high sensitivity is indicated, no attempt was made to use larger gaps in seeking the non-initiation threshold. An oscillogram illustrating the continuous response of the rate probe to a high-

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\*Reference to specific brands of equipment made for identification only and does not imply endorsement by the Bureau of Mines.

TABLE 2

## Shock sensitivity data on condensed-phase NO

Container: 26.64-mm-ID by 3.38-mm-wall steel pipe

Booster: tetryl -  $50 \times 10^{-3}$ -kg (41.28 mm in diameter by 25.40 mm long)

Approximate charge length (mm)	Attenuator length (mm)	Temperature (K)	Results*
<i>A. Boiling NO</i>			
380	0.08 (Teflon)	121	HVD (5100)
380	0.08 (Teflon)	121	HVD (5500)
	101.6 (Plexiglas)		
380	0.08 (Teflon)	121	HVD (5500)
	254.0 (Plexiglas)		
<i>B. Nonboiling liquid NO</i>			
230	1.27 (steel)	114	HVD (5400)
	127.0 (Plexiglas)		
300	1.27 (steel)	114	HVD (5300)
	254.0 (Plexiglas)		
<i>C. Solid NO</i>			
510	1.02 (steel)	78	HVD (6000)
510	1.27 (steel)	78	HVD ( — )
	25.4 (Plexiglas)		
510	1.27 (steel)	78	HVD (6100)
	50.8 (Plexiglas)		
510	1.27 (steel)	78	HVD (6100)
	76.2 (Plexiglas)		
510	1.27 (steel)	78	NI
	127.0 (Plexiglas)		

\* Numerical values in parentheses are the average detonation rates (m/s). HVD, high-velocity detonation. NI, noninitiation.

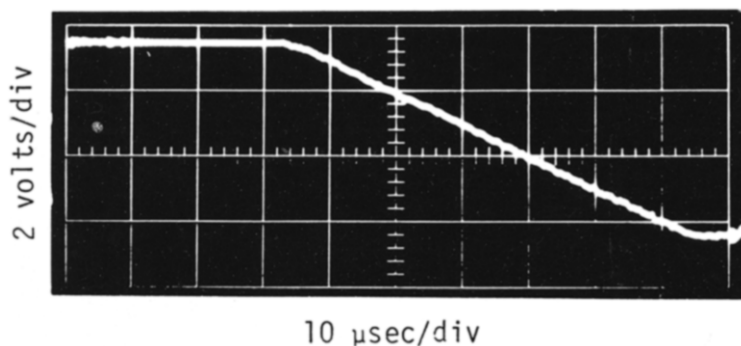


Fig. 3. Response of rate probe to a high-velocity detonation in boiling NO (5500 m/s).

velocity detonation in boiling NO is presented in Fig. 3.

In a related test, boiling NO precooled with liquid  $N_2$ , contained in an insulated glass beaker 51 mm in diameter and 102 mm deep, positioned on top of a 25-mm-thick steel witness plate, detonated at high velocity when initiated with a No. 8 commercial electric blasting cap. The detonator, covered with sheet polyethylene, was immersed approximately 51 mm into the sample.

### Nonboiling liquid NO

Nonboiling liquid NO was prepared in a closed system by condensing the gas as a solid in a 26.64-mm-ID by 3.38-mm-wall steel pipe 914 mm long (sealed at the bottom with a 1.02-mm steel diaphragm), immersed in an isopentane (2-methylbutane) bath, surrounded by a liquid nitrogen bath. The concentric baths were surrounded by foamed plastic insulation. Details of the arrangement are shown in Fig. 4. Upon completion of the transfer of NO gas to the 26.64-mm-ID by 3.38-mm-wall steel pipe condenser and its solidification, the liquid  $N_2$  was dumped. The NO was permitted to warm up slowly from 78 K to the first plateau of 110 K, the melting point of NO. The liquid charge was fired when the temperature reached the second plateau of 114 K, the melting point of the isopentane bath. Temperatures were measured by copper-constantan thermocouples positioned at the 152-mm level on the inside, and at the 76-mm and 229-mm levels on the outside of the steel charge container.

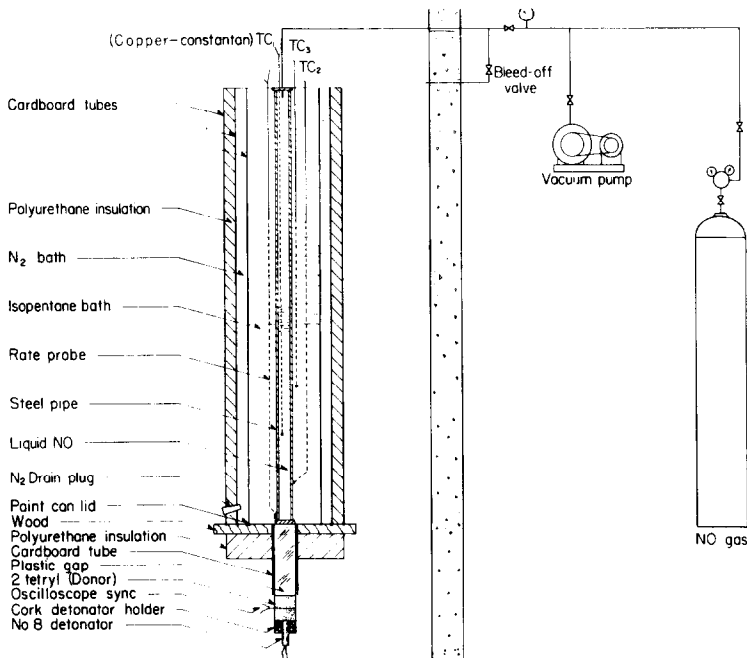


Fig. 4. Arrangement for preparation and detonation of nonboiling NO.

The results of the experiments on nonboiling liquid NO at 114 K and  $0.100 \text{ MN/m}^2$  pressure are given in Table 2 (series B). Detonations with velocities of 5400 and 5300 m/s were obtained in 230- and 300-mm-long charges at 128- and 255-mm gaps, respectively. An oscillogram illustrating the continuous response of the rate probe to a high-velocity detonation in nonboiling NO is presented in Fig. 5. The section of the curve having the greatest slope represents the detonation velocity over the liquid NO-filled portion of the chamber, and the section of lesser slope probably resulted from an inert shock propagating beyond the fill level of NO in the cooling bath of isopentane.

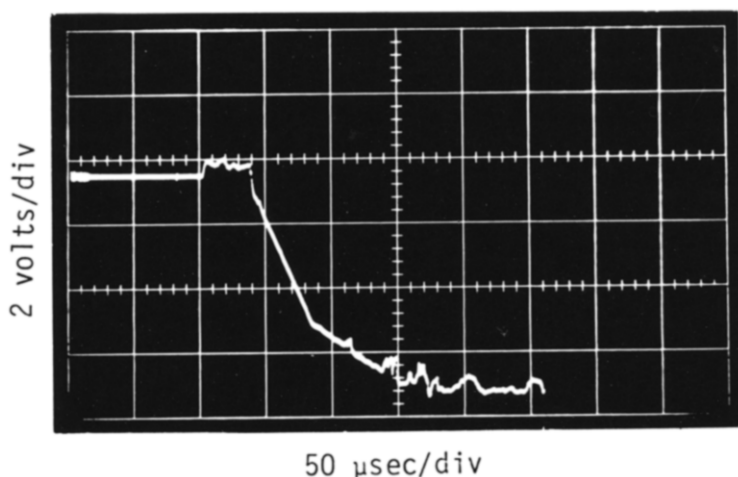


Fig. 5. Response of rate probe to a high-velocity detonation in nonboiling NO (5300 m/s).

### *Solid NO*

Solid NO was also prepared in a closed system by condensing the gas in a 914-mm-long, 26.64-mm-ID by 3.38-mm-wall steel pipe, immersed in a liquid  $\text{N}_2$  bath, and fired at 78 K. A copper-constantan thermocouple at the 406-mm level inside the steel container was used to measure the temperature of the charge. A charge of solid NO ready for firing is shown in Fig. 6a. The extent of damage to the steel pipe containers after a detonation and after a noninitiation in solid NO is presented in Fig. 6b. The initiation was at the bottom of the charge containers (center and right); the small fragments are from that portion of the tube containing the solidified NO; the large fragments and intact tube section are from the unfilled portion.

The results of the experiments with solid NO at 78 K are also given in Table 2 (series C). When boosted with a  $50 \times 10^{-3} \text{ kg}$  tetryl donor, solid NO in charge lengths of approximately 510 mm, detonated at a velocity of approximately 6100 m/s at 1.0-, 26.7-, 52.1-, and 77.5-mm gaps; a failure occurred with a 128.3-mm gap. Oscillograms showing the responses of the rate probe to a high-velocity detonation and to a noninitiation in solid NO are



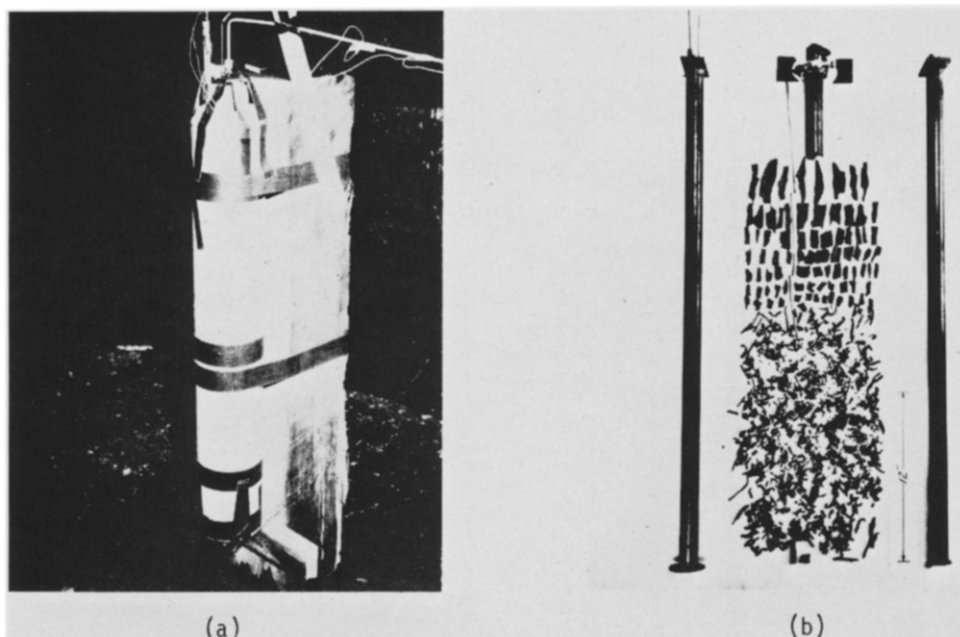


Fig. 6. (a) Bombproof setup for a firing of solid NO. (b) Extent of damage to 26.64-mm-ID by 3.38-mm-wall steel pipe containing solid NO. Left, before firing; center, detonation; right, noninitiation using 127-mm gap.

given in Fig. 7a, b. In Fig. 7a, the discontinuities in the trace are due to probe response at the initiated end that may represent instabilities during initiation and growth to a steady-state detonation; however, a steady velocity of 6000 m/s was observed over the downstream half of the charge.

#### *Nitrous oxide, nitrogen tetroxide, carbon monoxide, and ethylene*

Using the techniques developed for nitric oxide, the detonation characteristics of nitrous oxide as a solid and nonboiling liquid, nitrogen tetroxide and carbon monoxide as nonboiling liquid, and ethylene as a nonboiling liquid and as a gas at high pressure, were briefly explored. These materials are of interest because of their simple molecular structure and the fact that exothermal reactions for the neat materials might be anticipated on the basis of thermochemical considerations. The results of these experiments are summarized in Table 3.

Solid  $\text{N}_2\text{O}$  (136 K,  $0.100 \text{ MN/m}^2$ ) and nonboiling liquid  $\text{N}_2\text{O}$  (197 K,  $0.400 \text{ MN/m}^2$ ) confined in 26.64-mm-ID by 3.38-mm-wall steel pipe failed to initiate when shocked with a  $50 \times 10^{-3}$  kg tetryl donor coupled to a 1.27-mm-thick steel attenuator that sealed the container. Nonboiling liquid  $\text{N}_2\text{O}_4$  (273 K,  $0.100 \text{ MN/m}^2$ ) also failed to initiate when tested under the same conditions. Nonboiling liquid CO (78 K,  $0.100 \text{ MN/m}^2$ ) failed to initiate in both a 26.64-mm-ID by 3.38-mm-wall steel pipe with a  $50 \times 10^{-3}$  kg tetryl donor

TABLE 3  
Shock sensitivity of materials

Container (steel pipe)	Tetryl booster weight ( $10^{-3}$ kg)	Attenuator length (mm)	Temperature (K)	Pressure (MN/m <sup>2</sup> )	Results*
<i>A. Nitrous oxide (N<sub>2</sub>O)</i>					
26.64-mm ID by 3.38-mm wall	50	1.27 (steel)	136 (solid)	0.100	NI
26.64-mm ID by 3.38-mm wall	50	1.52 (steel)	197 (nonboiling liquid)	0.400	NI
<i>B. Nitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>)</i>					
26.64-mm ID by 3.38-mm wall	50	0.08 (polyethylene)	273 (nonboiling liquid)	0.100	NI
<i>C. Carbon monoxide (CO)</i>					
26.64-mm ID by 3.38-mm wall	50	1.27 (steel)	78 (nonboiling liquid)	0.100	NI
49.25-mm ID by 5.54-mm wall	350	1.27 (steel)	78 (nonboiling liquid)	0.100	NI
<i>D. Ethylene (C<sub>2</sub>H<sub>4</sub>)</i>					
26.64-mm ID by 3.38-mm wall	50	1.52 (steel)	153 (nonboiling liquid)	0.100	NI
42.90-mm ID by 8.71-mm wall	20	1.52 (neoprene)	293 (gas)	41.5	NI

\* NI, noninitiation.

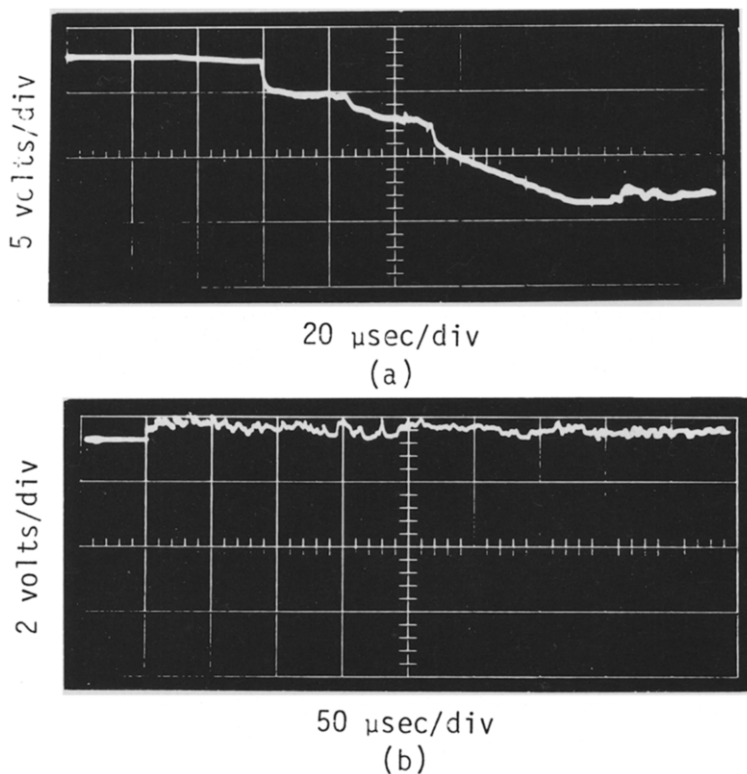
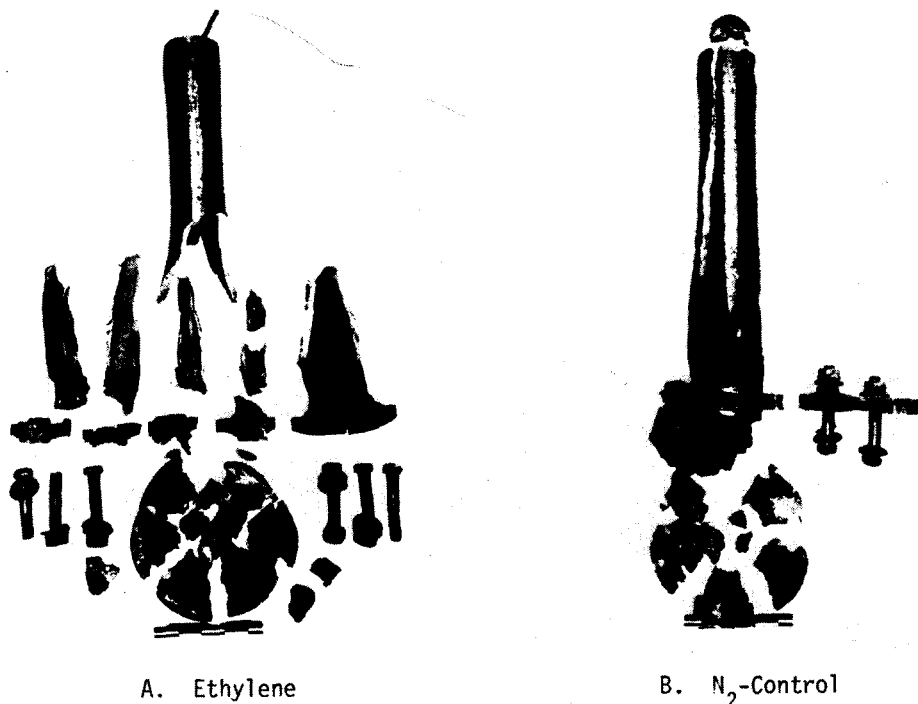


Fig. 7. Response of rate probes: (a) high-velocity detonation in solid NO (6000 m/s); (b) noninitiation in solid NO with a 127-mm Plexiglas gap.

and a 1.27-mm steel attenuator, and a 49.25-mm-ID by 5.54-mm-wall steel pipe using a  $350 \times 10^{-3}$  kg tetryl donor and a 1.27-mm steel attenuator.

Nonboiling liquid ethylene (153 K,  $0.100 \text{ MN/m}^2$ ) also failed to initiate in 26.64-mm-ID by 3.38-mm-wall steel pipe using a  $50 \times 10^{-3}$  kg tetryl donor. Since there are certain industrial chemical processes that involve high-pressure gas-phase ethylene, an additional test was conducted with gas-phase ethylene at  $41.5 \text{ MN/m}^2$  and 293 K. The gas was contained in a 42.90-mm-ID by 8.71-mm-wall steel pipe 381 mm long. An initiation source consisting of a  $20 \times 10^{-3}$  kg tetryl booster was placed inside the vessel. To avoid problems associated with high-pressure electrical feed-throughs and possible malfunctioning of electric detonators at high pressure, a commercial-shaped charge, "Jet-tapper", placed outside the container, was used to initiate the tetryl booster by piercing the 12.7-mm-thick steel-end cap used to seal the vessel. The effectiveness of the Jet-tapper in initiating the tetryl booster through the steel-end cap was verified in trials conducted at ambient pressure and at  $41.5 \text{ MN/m}^2$  using nitrogen gas.

The damage to the steel container used in a trial with  $\text{C}_2\text{H}_4$  at  $41.5 \text{ MN/m}^2$



A. Ethylene

B. N<sub>2</sub>-Control

Fig. 8. Damage to pressure vessels: (a) ethylene gas and booster; (b) nitrogen gas and booster.

is shown in Fig. 8a; for comparison purposes, Fig. 8b shows the results of a control firing using nitrogen gas at  $37.3 \text{ MN/m}^2$  and the same initiation system used in the ethylene test. An explosive reaction appears to have taken place in the ethylene near the booster charge. Since the downstream end of the container remained intact, the occurrence of a propagating detonation in the material can be ruled out. This follows from the fact that at an initial pressure of  $41.5 \text{ MN/m}^2$ , the detonation of ethylene would produce pressures of the order of  $700 \text{ MN/m}^2$ , which is more than adequate to rupture the heavy wall steel container. A slower combustion-type reaction of the type described by Scott [5] for neat ethylene at elevated pressures and the not unreasonable assumption that the reaction was vented and possibly quenched before completion could account for the tube damage.

### Conclusions

Nitric oxide is a material that detonates in all three phases. Detonations can be initiated in gaseous NO at both ambient and elevated pressures, but rather substantial energies are required, especially at low pressures. The effect of initial pressure on the minimum charge weight required to initiate detonation varies as the inverse first power of the pressure. In card-gap tests with

liquid NO, high-velocity detonations could be initiated using gaps as long as 254 mm; experience has shown [6] that materials with gap values of 254 mm or more are comparable to nitroglycerin in sensitivity to weak shock waves. Solid NO was observed to be less sensitive than the liquid, but still had gap values in excess of 76.2 mm, which is characteristic of materials having moderately high sensitivity. Experiments with relatively small-diameter charges showed that solid and liquid  $N_2O$  and liquid  $N_2O_4$ , CO, and  $C_2H_4$  were not detonable and gave no indication of energy release in the geometries tested. Experiments with gas-phase ethylene at elevated pressures showed some energy release but no evidence of sustained detonation in the charge diameters investigated.

## References

- 1 R.O. Miller, "Explosions in Condensed Phase Nitric Oxide", *Ind. Eng. Chem. Proc. Design and Development*, 7 (1968) 590.
- 2 J. Ribovich, R.W. Watson and F.C. Gibson, Instrumented Card Gap Test. *AIAA Journal*, 6 (1968) 1260.
- 3 D.S. Burgess, J.N. Murphy, N.E. Hanna and R.W. Van Dolah, Large-Scale Studies of Gas Detonations, BuMines RI 7196, November 1968, p. 53.
- 4 E.L. Litchfield, Marilyn L. Hay and David J. Cohen, Initiation of Spherical Detonation in Acetylene—Oxygen Mixtures, BuMines RI 7061, December 1967, p. 6.
- 5 G.S. Scott, R.E. Kennedy, I. Spolan and M.G. Zabetakis, Flammability Characteristics of Ethylene, BuMines RI 6659, 1965, p. 10.
- 6 R.W. Watson, Card-Gap and Projectile Impact Sensitivity Measurements, A Compilation. BuMines IC 8605, 1973, p. 12.