Detonations in mixtures containing nitrous oxide

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Abstract: We report on our experimental studies and chemical kinetic modeling of detonations in nitrous oxide (N_2O)-fuel-diluent systems. Detonation cell width measurements by the soot foil method were performed for mixtures containing hydrogen, nitrous oxide, nitrogen, oxygen, methane and ammonia in a 280-mm diameter detonation tube. A set of detailed chemical reaction mechanisms were compared to shock tube data sets and then applied to the prediction of reaction zone length using the ZND model and correlation to cell width.

Key words: detonation, nitrous oxide, chemical kinetics

1. Introduction

Detonation hazards in mixtures of fuel, nitrous oxide and air are a potential concern in nuclear waste storage facilities. Chemical and radiolytic generation of gases can create explosive mixtures under certain conditions. In order to evaluate the potential for detonation, some quantitative characterization of the detonation hazard is needed. The most readily accessible measure of detonation hazard is the detonation cell width, which can be measured in laboratory experiments and related by empirical correlations (Lee 1984) to other figures of merit such as initiation energy and critical tube diameter.

Although a great deal of information is available on detonation hazards in hydrocarbon-oxygen-diluent mixtures (Kaneshige et al. 1997, Westbrook and Urtiew 1984), relatively little information is available on mixtures containing nitrous oxide. We have systematically collected data on cell width in mixtures containing the fuels hydrogen, methane, and ammonia, and the oxidizers oxygen or nitrous oxide, and added nitrogen or air.

Detonation cell width measurements were carried out in a stainless steel detonation tube, 7.3-m long and 280-mm internal diameter. The gas composition in this tube is created by the method of partial pressures after evacuating the tube. Detonation is initiated by a combination of an exploding wire and a short section of an oxygen-acetylene mixture. Detonation wave speed measurements indicate that values within 2% of the Chapman-Jouguet (CJ) value can be obtained routinely away from the limits of detonability. Detonation cells were recorded on a sooted sheet of aluminum (0.6-m x 0.9-m) rolled up inside the tube and riveted onto a stiffening ring. Detonation cell widths were determined by hand measurement on the flattened sheets. Typically 10 measurements were made with the average, maximum and minimum values reported. Initial conditions for most mixtures were 1 bar pressure and 295 K. In some cases, the initial pressure was limited to subatmospheric values due to the design limits of the tube. The facility, experiments, and simulation results are described in detail in Akbar et al. 1997.

2. Cell Width Measurements

Detonation cell widths were measured for each fuel: hydrogen, methane and ammonia in stoichiometric combination with nitrous oxide and for reference, oxygen. These mixtures were diluted by adding nitrogen and in some cases, air. Computations of the CJ velocity indicate that for the purpose of computing detonation speed and post-shock thermodynamic state, the oxygen in the air is essentially inert. Detonation CJ wave speeds for mixtures diluted with 70 to 80% air are about 2% lower than those diluted with N_2 alone. The decrement is due to the lower dissociation energy of O_2 compared to N_2. Obviously this conclusion is only relevant for stoichiometric and fuel-lean mixtures and even for these mixtures, it is still possible to have effects due to the difference in reaction rates of O_2 and N_2O with the fuel molecules and intermediates.

The detonation velocities of stoichiometric mixtures are higher when O_2 is used as the oxidizer than N_2O. This is because the dissociation of N_2O generates N_2 which dilutes the combustion products, offsetting the energy release due to the positive heat of formation of N_2O. For fuel-rich and stoichiometric mixtures, this makes O_2 a more energetic oxidizer than N_2O. However for fuel-lean mixtures, the energy release from N_2O decomposition plays an essential role and lean mixtures containing N_2O can be much more detonable than those using O_2 as an oxidizer.

The results of our measurements and in some cases,

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those of other researchers are given in Figs. 1-5. The initial pressure for each datum or data series is shown in the legend; when a range of pressures are shown, the original data (Akbar et al. 1997) should be consulted for values corresponding to individual data points.

All of these cases show that as the amount of N_2 or air is increased, the cell width increases. This is due to the reduction in energy per unit mass of the reactants with increasing dilution causing the CJ detonation velocity to decrease, resulting in lower postshock temperatures and longer reaction times. It is well established (Shepherd 1986, Westbrook and Urtiew 1984) that the detonation cell width is approximately proportional to the induction time so that this effect accounts for the increase in cell width with increasing amounts of N_2 or air. These trends are consistent with those previously observed in experiments for fuel-oxygen systems.

Data for the stoichiometric H_2-N_2O system are shown in Fig. 1. These data show the general trend of increasing cell width with increasing amount of added nitrogen or air. It is difficult to discern a difference between mixtures with added N_2 or air given the range of values observed for cell width.

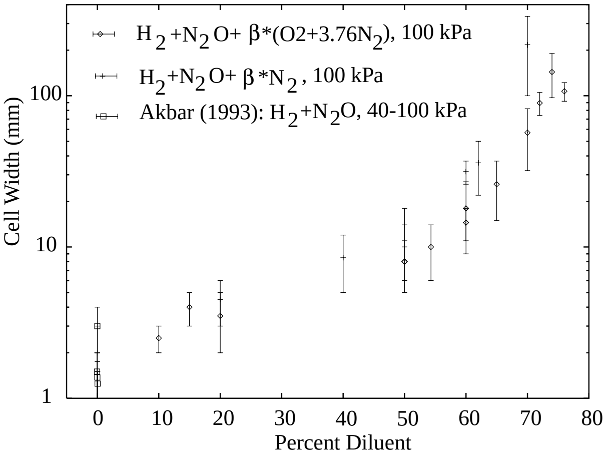

Figure 1. Measured cell width for stoichiometric H_2-N_2O mixtures vs. N_2 or air percentage.

Cell widths for CH_4-O_2 detonations were measured (Fig. 2) in order to validate our data. Our results are consistent with those of previous researchers (Manzhalei et al. 1974, Knystautas et al. 1984, Moen et al. 1984, Abid et al. 1991, Beeson et al. 1991) for CH_4-air detonations (75.2% N_2) and for CH_4-O_2 detonations. Data for CH_4-N_2O mixtures (Fig. 3) over a range of initial presures (57 to 102 kPa) indicate at most a slight difference between air and nitrogen addition. The cell width for O_2 is slightly smaller than with N_2O as the oxidizer.

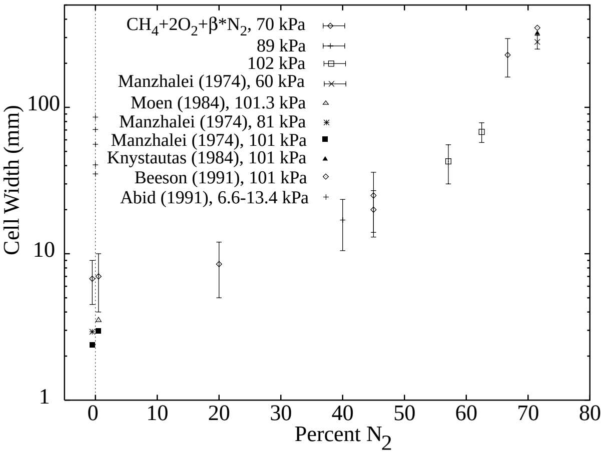

Figure 2. Measured cell width for stoichiometric CH_4-O_2 mixtures vs. N_2 or air percentage.

Cell widths for NH_3-O_2-N_2 mixtures were measured in our lab and compared to previous unpublished data of Bennett 1986 (Fig. 4). Although our initial pressures are lower than Bennett's, the two sets of data are in reasonable agreement. In contrast to the case of H_2 and CH_4, cell widths for the stoichiometric NH_3-N_2O system (Fig. 5) are substantially smaller than for the NH_3-O_2 system at the same concentration of N_2 or air. This suggests that a direct pathway exists for reaction between NH_3 and N_2O. Further evidence of this is given subsequently in the comparison of reaction zone length and cell width.

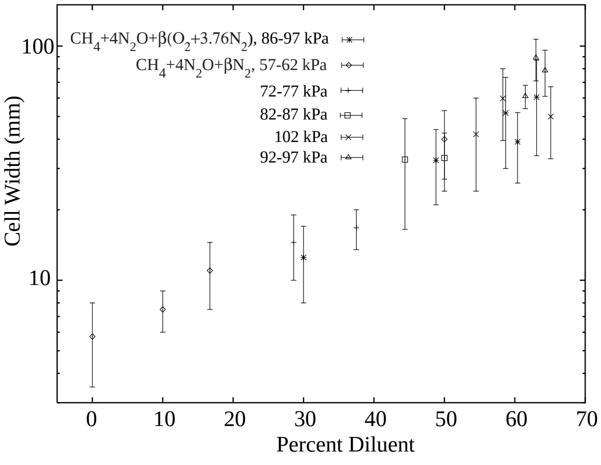

Figure 3. Measured cell width for stoichiometric CH_4-N_2O mixtures vs. N_2 or air percentage.

3. Chemical Reaction Modeling

3.1. Validation

The cell width measurements we have carried out are for a limited range of mixtures and initial conditions. In explosion hazard analyses, it is often necessary to consider a much wider range of initial conditions and compositions than can be practically studied in the

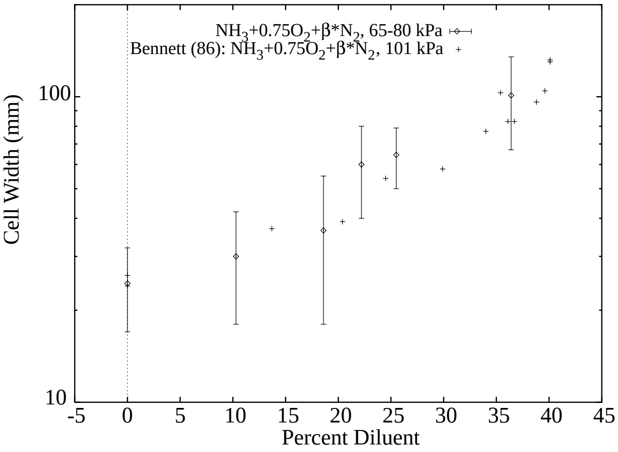

Figure 4. Measured cell width for stoichiometric NH_3-O_2 mixtures vs. N_2 or air percentage.

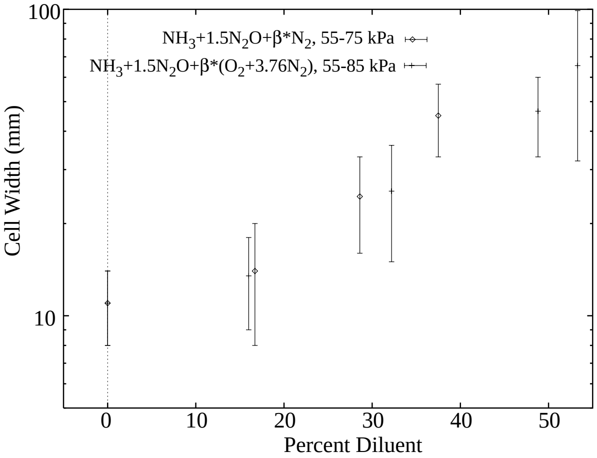

Figure 5. Measured cell width for stoichiometric NH_3-N_2O mixtures vs. N_2 or air percentage.

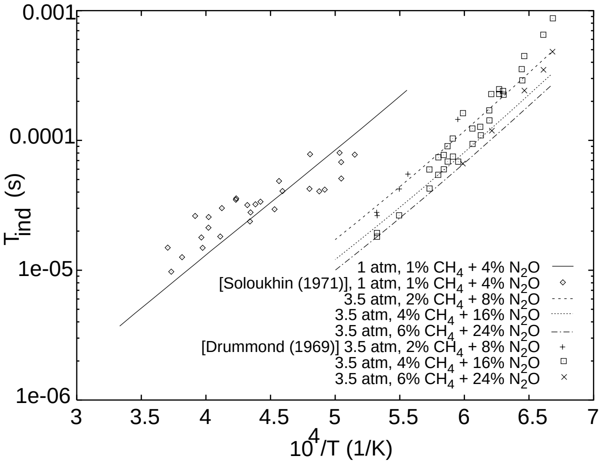

Figure 6. Validation of GRI-Mech 2.11 reaction mechanism against CH_4-N_2O-diluent shock tube induction time data.

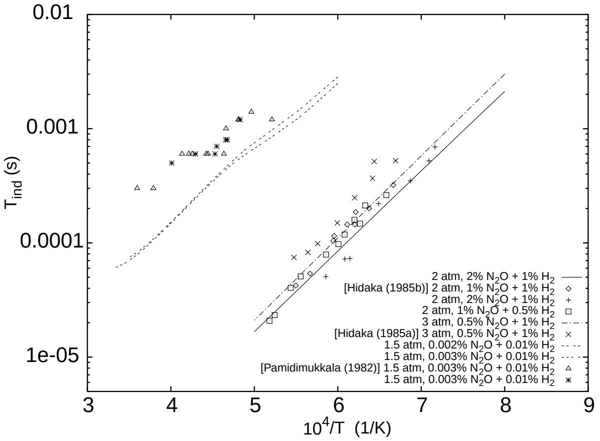

Figure 7. Validation of GRI-Mech 2.11 reaction mechanism against H_2-N_2O-diluent shock tube induction time data.

lab. For this purpose, chemical kinetic modeling has proven (Shepherd 1986, Westbrook and Urtiew 1984) to be very useful for estimating cell width and other detonation parameters. However, it is necessary to validate a reaction mechanism before it can be used for this purpose.

An extensive comparison (Akbar et al. 1997) between the published shock tube experiments and computations based on previously published mechanisms has been carried out for all three fuels. Examples of comparisons between measured and computed induction times are given in Figs. 6-8. The GRI Mech-2.11 (Frenklach et al. 1995) was the most accurate mechanism for CH_4 and H_2 simulations. Comparisons to the shock tube data of Soloukhin (1971) and Drummond (1969) for CH_4-N_2O-Ar mixtures are given in Fig. 6. Comparisons with data of Hidaka (1985a,b) and Pamidimukkala (1982) for H_2-N_2O-Ar mixtures are given in Fig. 7. A modified version of the Miller and Bowman (1989) mechanism was found to be the most accurate for NH_3 mixture simulations. Comparisons with data of Soloukhin (1971) and Drummond (1967) for NH_3-N_2O-Ar mixtures are shown in Fig. 8. Details of the modifications of the Miller-Bowman mechansim, results for other mechanisms, and additional shock tube data are given in Akbar et al. 1997.

3.2. ZND Computations

ZND reaction zone lengths were computed as described in Shepherd (1986) using the two reaction mechanisms discussed above. The correlation between cell width λ and reaction zone length Δ_σ is shown in Figs. 9-12. Although the traditional analysis (Shepherd 1986, Westbrook and Urtiew 1984) is to take the $\lambda = A\ \Delta$ with A an empirically determined parameter, we find a power law $\lambda \propto \Delta^n$ relationship. The exponent n varies between 0.4 and 1.3

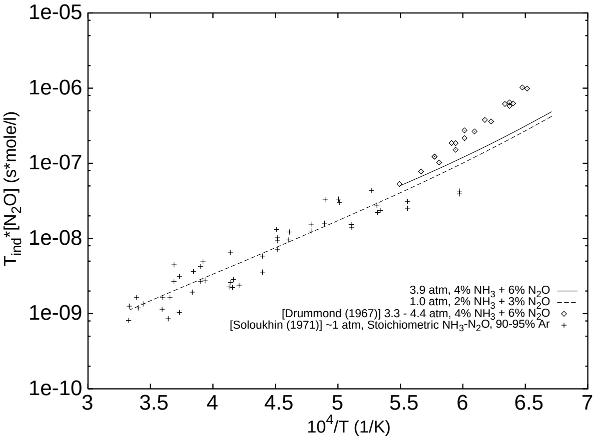

Figure 8. Validation of Miller-Bowman (1989) reaction mechanism against NH_3-N_2O-diluent shock tube induction time data.

depending on the fuel type and oxidizer. The results for H_2 (Fig. 9) and CH_4 (Fig. 10 and 11) indicate the exponents are quite different for O_2 and N_2O cases. The results for NH_3 (Fig. 12) indicate that although the exponents are similar, the curves are substantially displaced for O_2 and N_2O cases. Clearly there are additional factors associated with the specific chemical systems that must account for these differences. Effective activation energies, ratio of specific heats and detonation Mach number are some of the parameters that are currently being investigated.

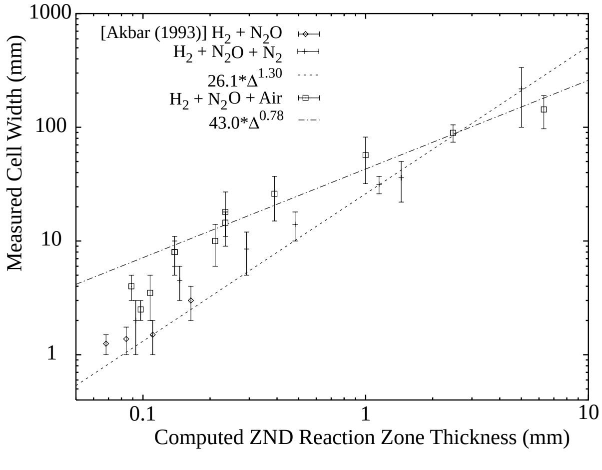

Figure 9. Measured cell width for H_2-N_2O-N_2 and H_2-N_2O-air mixtures vs. computed ZND reaction zone length; initial conditions: 70 to 100 kPa and 295 K.

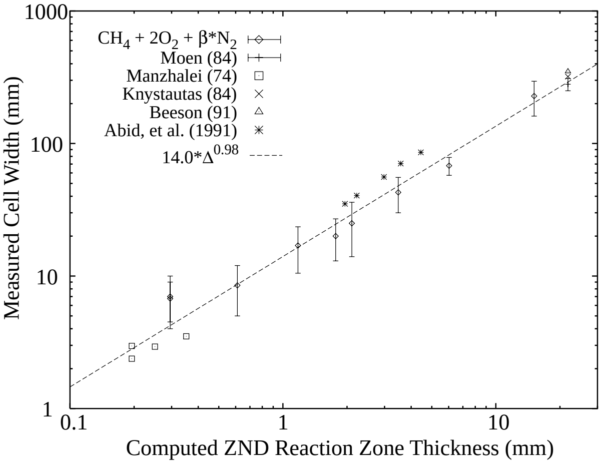

Figure 10. Measured cell width for CH_4-O_2-N_2 mixtures vs. computed ZND reaction zone length; initial conditions: 100 kPa and 295 K.

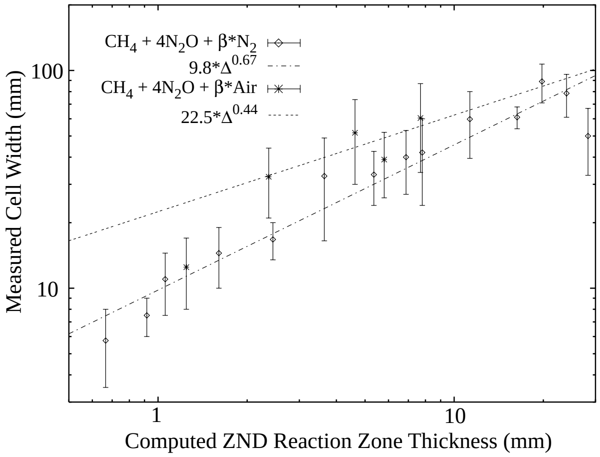

Figure 11. Measured cell width for CH_4-N_2O-N_2 and CH_4-N_2O-air mixtures vs. computed ZND reaction zone length; initial conditions: 100 kPa and 295 K.

4. Detonation of Nitrous Oxide and Hydrogen

The H_2-N_2O system has been studied in detail. One set of experiments (Fig. 1) has examined the detonation properties of stoichiometric H_2-N_2O mixtures diluted with air or N_2. Another set of experiments (Pfahl et al. 1998) has examined the effect of equivalence ratio variation (Fig. 13). The cell width vs. equivalence ratio curve has the familiar "U" shape with a minimum near stoichiometric conditions, but there are some significant differences between lean H_2-N_2O and lean H_2-O_2 mixtures. Since N_2O can exothermically decompose even in the absence of fuel, detonation velocities of lean H_2-N_2O mixtures can be much higher than the corresponding H_2-O_2 mixtures at the same equivalence ratio and diluent amount. The higher detonation velocity results in higher post-shock temperature, smaller reaction zone lengths, and smaller cell widths.

It may even be possible for pure N_2O to sustain a detonation if the decomposition rate is sufficiently high. However, for extremely lean mixtures, the decomposition of N_2O is limited by the lack of hydrogen-

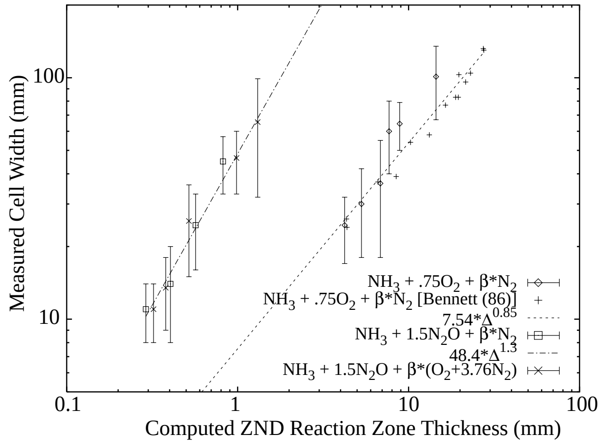

Figure 12. Measured cell width for NH_3-N_2O-air or -N_2 and NH_3-O_2-air or -N_2 mixtures vs. computed ZND reaction zone length; initial conditions: 70 to 100 kPa and 295 K.

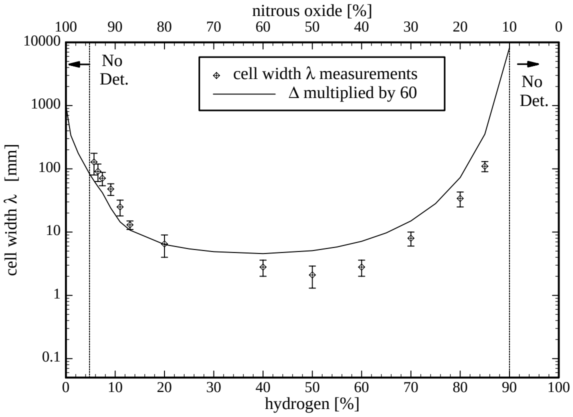

Figure 13. Cell width and reaction zone length for H_2-N_2O mixtures as a function of equivalence ratio.

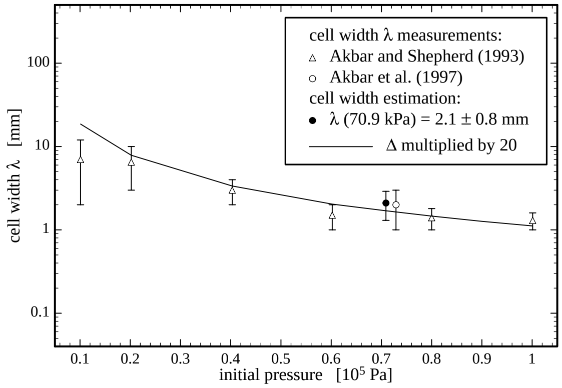

Figure 14. Cell width and reaction zone length for stoichiometric H_2-N_2O mixtures as a function of initial pressure.

atom bearing species, which are apparently required to catalyze the decomposition process. We were unable to produce detonations for less than 5% H_2 in our facility. Experiments with pure N_2O merely resulted in shock waves with little or no obvious decomposition. Estimates of the reaction zone length suggest that detonation of pure gaseous N_2O is not practical in typical laboratory test rigs.

The addition of small amounts of CH_4 and NH_3 to equimolar H_2-N_2O mixtures substantially increases the cell width. Adding 3% CH_4 increased the cell width by a factor of 3; adding 3% NH_3 increased the cell width by a factor of 6.

The dependence of cell width on pressure is shown in Fig. 14. Note that only a modest change in cell width is observed for a large variation in initial pressure. The normalized cell width is shown in Fig. 15 for H_2-N−2O mixtures and H_2-air mixtures. The value of λ_{min} was the minimum value of the cell width observed for a given mixture series. The minimum occurs close to the overall stoichiometric condition. Note how the lean H_2-N_2O mixtures are much more sensitive (smaller cell width) than hydrogen-air mixtures at the same equivalence ratio.

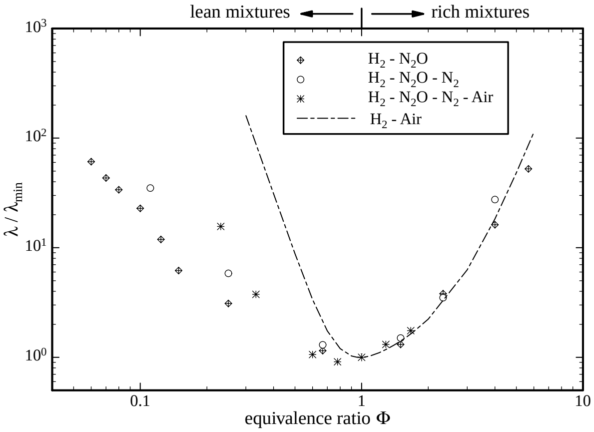

Figure 15. Comparison of normalized cell width for H_2-N_2O and H_2-air mixtures.

5. Summary

Detonation cell widths have been measured for three systems that were previously uncharacterized: H_2-N_2O, CH_4-N_2O, and NH_3-N_20. Comparision tests with oxygen as the oxidizer were also carried out. Representative values of the cell width at various dilutions are given in Table 1. Cell widths are slightly smaller for H_2 and CH_4 mixtures with O_2 as the oxidizer instead of N_2O. For NH_3 mixtures, the detonation cell width is substantially smaller with N_2O than with O_2 as the oxidizer. The undiluted NH_3 mixtures have substantially larger cell widths (one-order-of-magnitude) than either H_2 or CH_4 mixtures. Correlation of cell width with computed ZND reaction zone lengths resulted in power law dependencies (exponents between 0.4 and 1.3) rather than simple proportionalities.

Detonations in pure N_2O were not observed. Small amounts of H_2 were observed to catalyze the reaction while small amounts of CH_4 or NH_3 were inhibiting. For pure N_2O, cell widths over 1 m were extrapolated from the existing data. The lowest H_2 concentration at which detonation could be obtained for H_2-N_2O mixtures in our facility was at 5.7%, which had a cell width of 48 mm.

Table 1. Summary of measured and estimated cell width data for fuel-N_2O mixtures at $T_1 = 295$ K and $P_1 = 100$ kPa.

Mixture	Diluent	(%)	λ (mm)
H_2+1/2O_2	-	0	1.3-2.0
	N_2	55	10-15
H_2+N_2O	-	0	1.5
	N_2	62	36
	air	65	26
CH_4+2O_2	-	0	3
	N_2	72	300
CH_4+4N_2O	-	0	3(*)
	N_2	64	80
	air	60	50
NH_3+ 3/4O_2	-	0	16-25
	N_2	35	100
NH_3+ 3/2N_2O	-	0	6(*)
	N_2	38	34(*)
	air	53	60(*)

(*) Extrapolated from lower initial pressures

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References

Abid S, Dupre G, Paillard C (1991) Oxidation of gaseous unsymmetrical dimethylhydrazine at high temperatures and detonation of UDMH/O_2 mixtures. Prog. Astro. Aero., 153, 162–181.

Akbar R, Shepherd JE (1993) Detonations in N_2O-H_2-N_2-Air Mixtures. Report for Los Alamos National Laboratories.

Akbar R, Kaneshige M, Schultz E, Shepherd JE (1997) Detonations in H_2-N_2O-CH_4-NH_3-O_2-N_2 Mixtures. GALCIT Report FM97-3, California Institute of Technology, Pasadena, CA.

Beeson H, McClenagan R, Bishop C, Benz F, Pitz WJ, Westbrook C, Lee JHS (1991). Detonability of hydrocarbon fuels in air. Prog. Astro. Aero. 133, 19–36.

Bennett CA (1986, March) Personal communication. Detonation Test Results and Predictions for NH_3-O_2-N_2 Mixtures.

Drummond L (1967) Shock-initiated exothermic reactions III. the oxidation of hydrogen. Aust. J. Chem. 20, 2331–2341.

Drummond L (1969). Shock-induced reactions of methane with nitrous and nitric oxides. Bull. Chem. Soc. Japan 42, 285–289.

Frenklach MM, Wang H, Bowman C, Hanson R, Smith G, Golden D, Gardiner W, Lissianski V (1995) An Optimized Chemical Kinetic Model for Natural Gas Combustion. Technical Report, Gas Research Institute, also see http://www.gri.org.

Hidaka Y, Takuma H, Suga M (1985a). Shock-tube studies of N_2O decomposition and N_2O-H_2 reaction. Bull. Chem. Soc. Japan. 58(10), 2911–2916.

Hidaka Y, Takuma H, Suga M (1985b). Shock-tube study of the rate constant for excited OH* ($^2\Sigma^+$) formation in the N_2O-H_2 reaction. J. Phys. Chem. 89(23), 4903–4905.

Kaneshige MA, Shepherd JE, Teodorczyk A (1997) Detonation Database. GALCIT Report FM97-8, California Institute of Technology, Pasadena, CA. Also available as http://www.galcit.caltech.edu/detn_db/html/

Knystautas R, Guirao C, Lee JHS, Sulmistras A (1984). Measurement of cell size in hydrocarbon-air mixtures and predictions of critical tube diameter, critical initiation energy, and detonability limits. Prog. Astro. Aero., 94, pp. 23–37.

Lee JHS (1984) Dynamic Parameters of Gaseous Detonation. Ann. Rev. Fluid Mech. 16, 311-336.

Manzhalei V, Mitrofanov V, Subbotin V (1974). Measurement of inhomogeneities of a detonation front in gas mixtures at elevated pressures. Combust. Explos. Shock Waves (USSR) 10(1), 89–95.

Miller JA, Bowman C (1989) Mechanism and modeling of nitrogen chemistry in combustion. Prog. Energy Comb. Sci 15, 287-338.

Moen I, Funk J, Ward S, Rude G, Thibault PA (1984). Detonation length scales for fuel-air explosives. Prog. Astro. Aero., 94, pp. 55–79.

Pamidimukkala K, Skinner G (1982). Resonance absorption measurements of atom concentrations in reacting gas mixtures. VIII. rate constants for O+H_2=OH+H and O+D_2=OD+D from measurements of O atoms in oxidation of H_2 and D_2 by N_2O. J. Chem. Phys. 76(1), 311–315.

Pfahl U, Schultz E, Shepherd JE (1998) Detonation cell width measurement in H_2-N_2O-N_2-O_2-CH_4-NH_3- Mixtures. GALCIT Report FM98-5, California Institute of Technology, Pasadena, CA.

Shepherd JE (1986) Chemical Kinetics of Hydrogen-Air-Diluent Detonations, Prog. Astro. Aero. 106, 263-293.

Soloukhin R (1973). High-temperature oxidation of hydrogen by nitrous oxide in shock waves. 14th Symp. Int. Combust. Proc., pp. 77–82.

Westbrook CK and Urtiew PA. (1984) Use of Chemical Kinetics to Predict Critical Parameters of Gaseous Detonations, Combust. Explos. Shock Waves 19(6), 65-76.