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Detonation in Gaseous Isopropyl Nitrate Mixtures

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Detonations of gaseous mixtures containing isopropyl nitrate (IPN) were investigated in the GALCIT detonation tube (280 mm diameter, 7.3 m long). Measurements were made of detonation pressures, velocities and cell widths for a range of IPN-air mixtures. Tests were conducted for stoichiometric IPN-air at initial pressures ranging from 10 to 100 kPa, and equivalence ratio was varied between 0.3 and 3.0 for a series of tests at 1 bar initial temperature. To ensure full vaporization of the liquid fuel, tests were performed at an initial temperature of 373 K. Preliminary efforts have been made to interpret the results using a detailed chemical reaction mechanism based on previous work on nitrated hydrocarbons, including propellants and high explosives. The reaction mechanism is compared with existing shock tube data, and applied in a tentative investigation of the reaction zone structure.

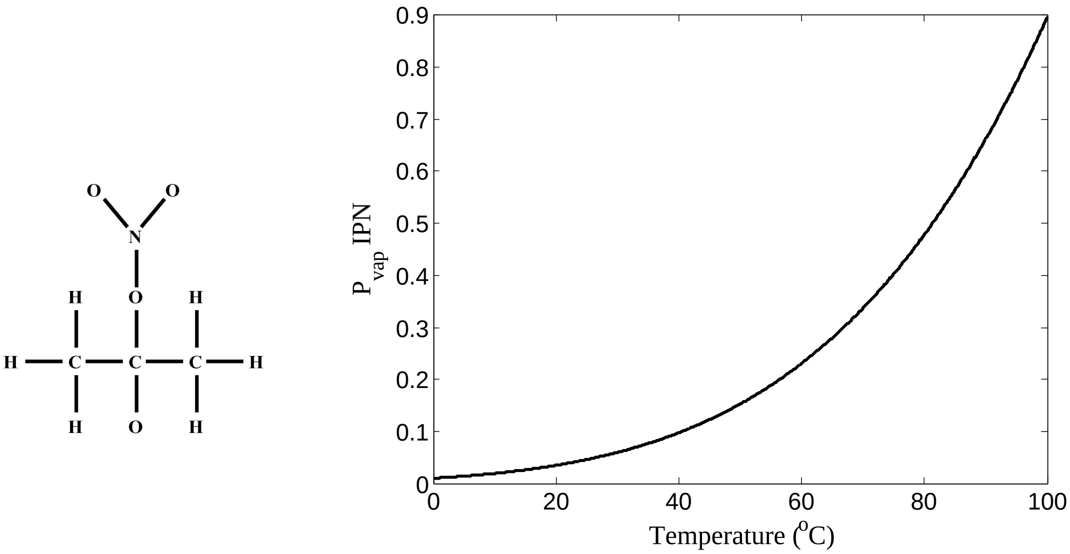
1 Introduction

Isopropyl Nitrate (IPN) is a flammable liquid at room temperature, and is of interest as a fuel additive [1, 2] and as a sensitizer in explosives [3]. There has been a great deal of work done on the ignition and detonation characteristics of the liquid fuel [4–8], as well as the thermal decomposition of the substance in its gas phase [9–16]. There has been very little work to date, however, investigating the properties of the gaseous fuel in detonations, and where this work has been done, it has been primarily concerned with the application of IPN as a sensitizing agent in hydrocarbon mixtures [3]. The purpose of the present study is to investigate the behavior of the pure material under the conditions of a detonation.

From an experimental point of view, the most accessible measure of the sensitivity of a given mixture is the detonation cell width. Beginning with the cell width, one may use empirical correlations to arrive at a wide variety of useful properties, such as initiation energy and critical tube diameter [17]. To this end, we have measured the detonation cell widths for mixtures of IPN, O_2, and N_2 for a range of equivalence ratios and initial pressures.

Of general interest is the effect of the nitrate group on combustion chemistry. Recently, Pinard et al. [18] added NO_2 in to propane mixtures in concentrations between 10 and 50% and found no effect on either the run up distance or detonation cell width, concluding that kinetic changes brought about by the presence of NO_2 are not significant to the initiation of detonations in a typical hydrocarbon fuel. Lamoureux and others [19–23] found that mixtures oxidized with NO_2, including rich mixtures of nitromethane, exhibit a double cellular detonation structure due to the heat release from NO_2 reduction occurring over two different time scales.

It is desirable to develop a reaction mechanism for gas phase IPN chemistry. This will allow us to perform calculations of the reaction zone thickness, which may then be correlated to the measured cell sizes and used as a predictive tool. For the present study, we have based our reaction mechanism on existing work on nitrated hydrocarbons. Once assembled, the mechanism is used in constant volume calculations for comparison with shock tube induction time data, and in one-dimensional ZND calculations to compute the reaction zone thickness for an idealized detonation.



(A) (B)

Figure 1: (A) IPN molecular structure. (B) IPN vapor pressure curve.

2 Experiments

2.1 Apparatus and Procedure

The tests were performed in the GALCIT Detonation Tube (GDT), shown schematically in Fig. 2. The tube is 7.3 m long, with an inner diameter of 280 mm. It is constructed of three sections of cast 304 stainless steel joined together by flanges and high strength fasteners [24]. Before each test, the tube is evacuated to a pressure of less than 50 mTorr. The tube is filled using the method of partial pressures, liquid IPN is injected into the tube through a septum, and N_2 and O_2 are added through a gas handling system. The mixture is circulated through the tube with a metal bellows pump during and after filling to ensure homogeneity.

Because some of the mixtures of interest had a high partial pressure of IPN, the tube was heated to ensure full vaporization of the fuel. The tube has been outfitted with a heating system totalling 13.75 kW in 19 independent zones of temperature monitoring and control. For the present series, the tube is heated to temperatures of around 100°C. Comparison with IPN vapor pressure data [25, 26] in Fig. 1B shows that this temperature is more than sufficient to ensure that the IPN is fully vaporized for the compositions of interest.

To initiate mixtures of low sensitivity, an oxy-acetylene driver is used. A slightly rich mixture of acetylene and oxygen is injected through a manifold of four tubes located at the ignition end of the GDT. Depending on the sensitivity of the test mixture, the driver gas was injected to a partial

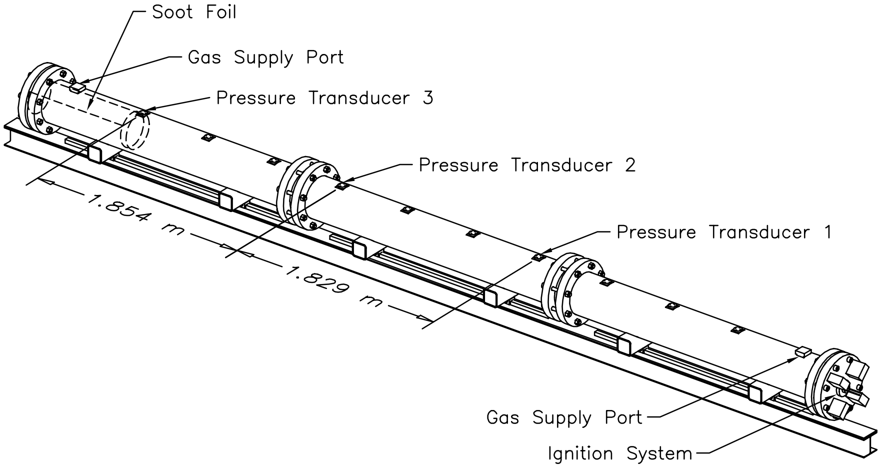


Figure 2: Schematic diagram of the GDT

pressure of between 2 and 8 kPa, controlled by adjusting injection time. Ignition is achieved via the explosion of a wire by capacitative discharge. A capacitor bank is charged to 9 kV and discharged through a length of thin copper wire. A fuller description and characterization of the driver system is found in Akbar et al. [24].

Prior to each shot, a sheet of aluminum (0.61 m by 0.91 m by 0.5 mm) is rolled along the long axis to the approximate inner diameter of the tube. For stiffness, a steel ring is riveted to one end of the rolled foil. The foil is then coated with a light layer of soot from a burning kerosene soaked rag, placed at the bottom of a closed ‘chimney’ containing the foil. For shots which result in a large amount of water formation, the foil is prepared prior to sooting by cleaning the inner side first with soap and water, and then with acetone, then applying a very thin coating of Dow Corning DC200 20 centistoke silicone oil, which prevents the water from washing away the soot tracks. Care must be taken with the application of the oil. It is typically applied in a very thin layer via a lightly soaked paper towel, and then the foil is wiped off with a clean paper towel. Too much oil results in poor contrast on the final soot foil. The sooted foil is then clamped into place just inside the downstream end of the tube.

The pressure and arrival time of the detonation are measured using PCB piezoelectric pressure transducers mounted along the tube, and this information is used to calculate the observed detonation velocity. When the detonation passes over the sooted foil, a cellular pattern is scoured into the soot. This pattern is associated with the instability of the detonation front, and the detonation cell width is the average width of the transverse wave spacing recorded on the foil. Significant uncertainty arises from the variation of cell size throughout the foil and the difficulty of identifying the precise locations of the triple point tracks. Typically, 10 measurements are made of the transverse distance between triple point tracks on each foil, and we report the minimum, maximum, and average of these measurements. Plotted cell widths are given “error bars” indicating the maximum and minimum measured widths to indicate the spread of the data. In general, uncertainty in cell width may be as high as 50%. It is important to note that this measurement is independent of confining geometry only when the cell width is much smaller than the tube diameter.

2.2 Results

Table 1 contains a summary of the shots performed to date. Primary studies have focused on IPN-air mixtures with varying initial pressures and IPN fractions. In the table, Φ is defined from Equation 1 below. Detonation velocities have been measured and the difference between the measured and Chapman-Jouguet (CJ) value (as obtained via STANJAN [27]) does not exceed 3%, and is usually within 1%. The measured cell cize corresponding to the sole existing point in the literature for an IPN-air detonation [3] has also been found to agree to within 3%.

$$\Phi C_3H_7NO_3 + 3.25(O_2 + 3.76N_2) \rightarrow products \tag{1}$$

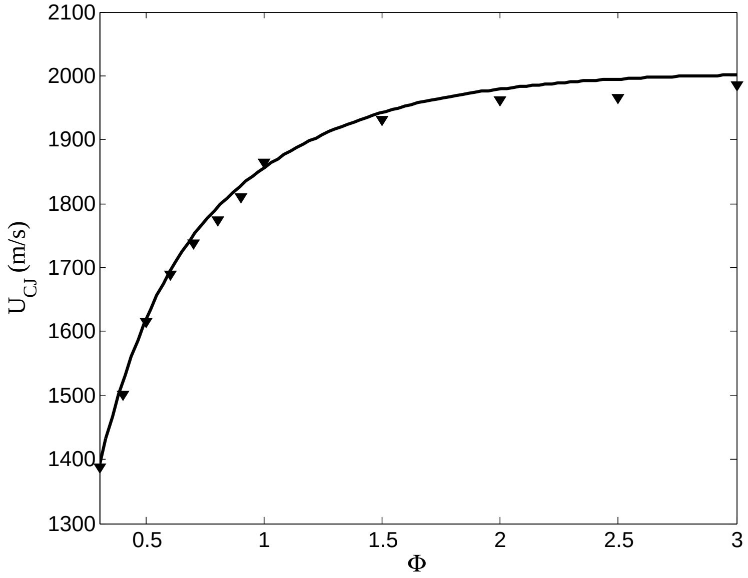
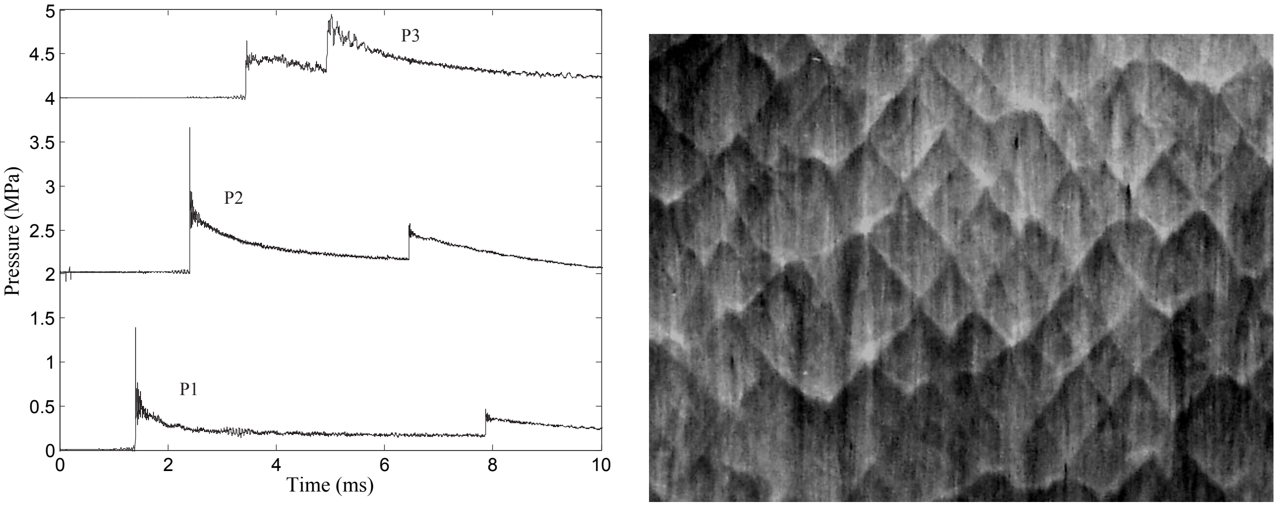


Figure 3: Comparison of measured detonation velocities with CJ velocities computed from STANJAN.

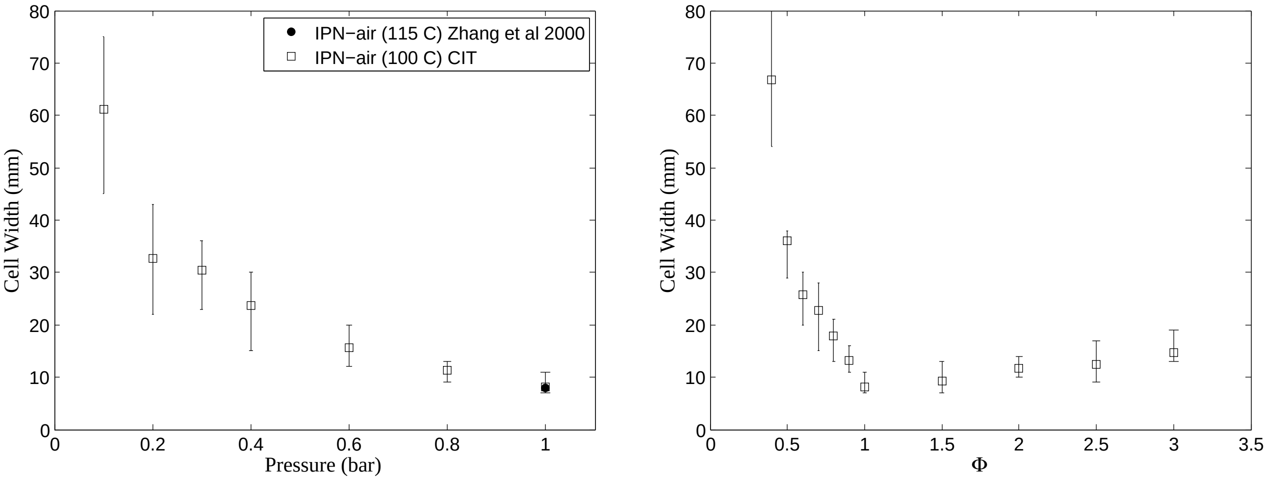
The measured detonation velocity is important in several ways. It allows us to verify the thermochemical data which we use, and informs us of a good test. When the detonation velocity is close to the CJ velocity, it indicates that the mixture composition is correct, the detonation has been successfully initiated, and that the tube is long enough that the initiation transient due to the explosion of the driver gas is not significant to the detonation in the region of interest (i.e. the soot foil). Figure 3 contains a comparison of the computed and measured detonation velocities for a range of mixtures.

Figure 4 contains a sample of the raw data obtained from a single experiment. Figure 5 contains detonation cell widths plotted against initial pressure and Φ for IPN-air detonations. In a series investigating the addition of IPN to hexane in mixtures with air, [3] obtained a single measurement of cell width for stoichiometric IPN-air at 1 bar initial pressure, which is included in the plot.



(A) (B)

Figure 4: Raw Data from shot 1944, data from pressure transducers. (A) Pressure Traces. (B) 20 by 15 cm region of soot foil.



(A) (B)

Figure 5: Detonation cell widths plotted vs. (A) initial pressure and (B) Φ.

3 Chemical Kinetics

The range of mixtures and conditions we are able to investigate in the lab is limited, and it is of interest to extend the applicability of the study to a broader range of conditions. Modeling of the chemical kinetics of a reacting system is useful for these purposes. For instance, it has been demonstrated that the reaction zone thickness computed from one dimensional kinetics calculations can be correlated to the detonation cell size [28, 29].

In order to reliably predict detonation cell widths from kinetics calculations, we must first develop a reaction mechanism for the mixture. The mechanism must then be validated against shock tube induction time measurements. Then it may be used to compute reaction zone thicknesses for correlation to experimental cell size data.

Previous work on reaction mechanisms for IPN combustion is scarce. There have been many efforts to measure the activation energy for gas phase decomposition at various conditions [9–11, 15, 25], studies of the decomposition products through mass and IR spectroscopy [12, 13], and Zaslonko [14] proposed a mechanism for the decomposition of methyl-, ethyl-, and propyl-nitrates including IPN.

The reaction mechanism was assembled based on previous work. The rate constant for IPN decomposition was taken from Zaslonko [14], the hydrocarbon sub-mechanism was taken from Curran et al. [30], and the nitrogen submechanism taken from Yetter et al. [31]. Two types of calculations which are of immediate interest are the solutions of the constant volume explosion, and steady 1-D (ZND) detonation equations. The pertinent differential equations are integrated in time, and property and reaction rate calculations are performed using Cantera [32].

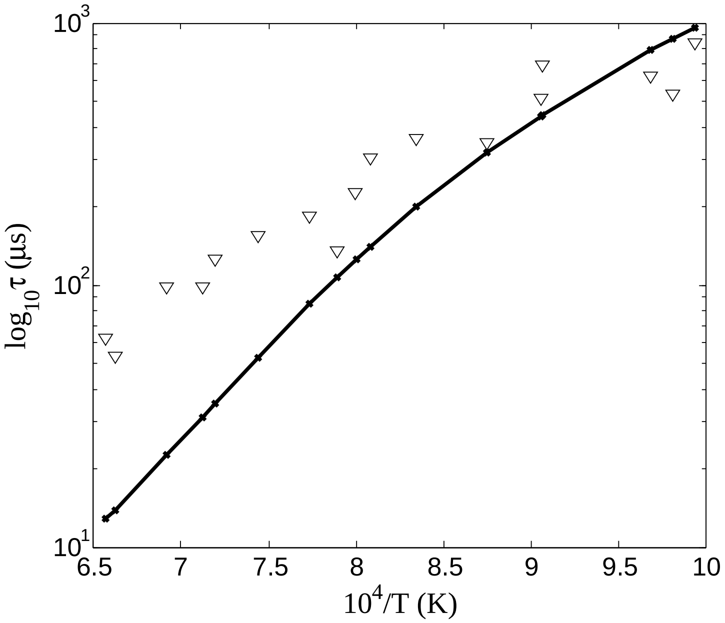


Figure 6: Comparison of constant-volume calculation with published shock tube data.

For validation of the mechanism, we are using shock tube data from Toland and Simmie [16]. They used a mixture of 1% IPN, 4% O_2 and 95 % Ar. Ignition delay times were reported for temperatures ranging from 1237-1510 K with final pressures of 3.5 kPa. Ignition delay time was defineded as the time corresponding to the maximum intensity of light on the wavelength of the chemiluminescent reaction of CO with O. To simulate this experiment, constant- volume calculations were run at these initial conditions and the ignition delay time was taken as the time of maximum CO concentration. Results of this comparison may be seen in Fig. 6. It should be emphasized that the mechanism is still under development, and all reported data from kinetics modeling is indication of a work in progress.

A problem with the use of shock tube data to validate a chemical mechanism for use with detonations is the fact that shock tubes are incapable of approaching the von Neumann conditions typical for detonations. In particular, post shock pressures are frequently much higher than are accessible

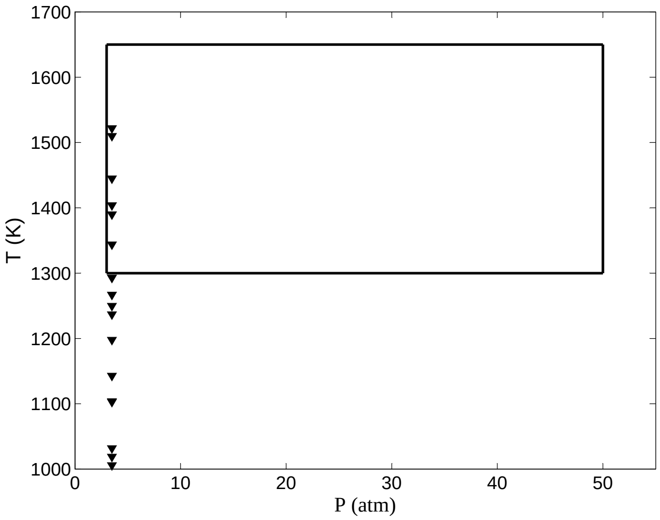
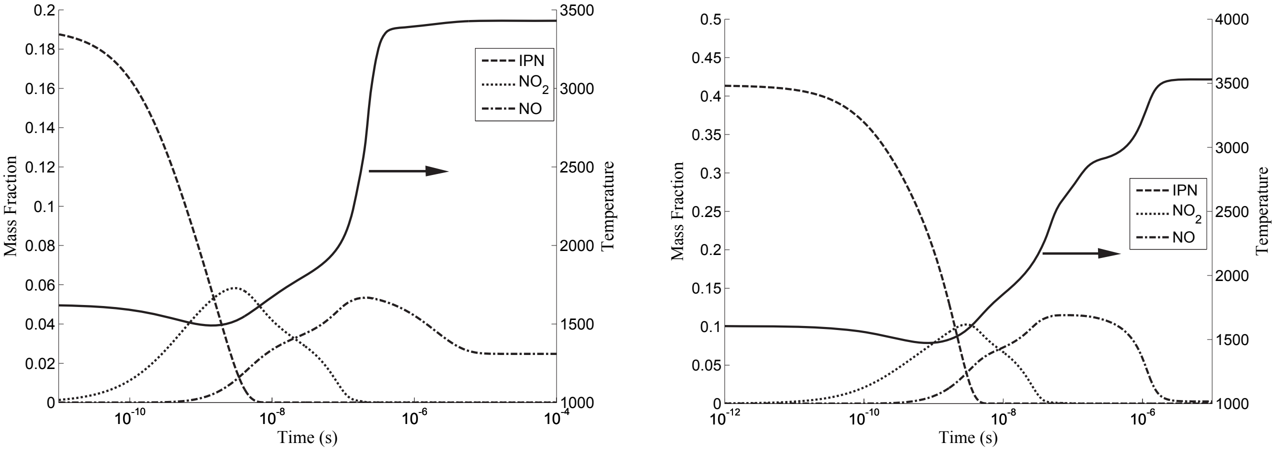


Figure 7: Points available from Toland and Simmie [16] plotted on top of the approximate envelope of post shock conditions in the present study.

in a shock tube. Figure 7 plots in pressure-temperature space the points reported in Toland and Simmie [16] and the envelope of post-shock conditions in the detonations we have observed in the lab.

As a preliminary step toward performing detonation calculations, we may model the detonation as a constant volume explosion following a shock. The CJ velocity is computed using realistic thermochemistry, and the jump conditions are used to get the state of the frozen reactant mixture after the shock. This state is then used as the initial condition in a constant-volume explosion calculation using detailed chemistry.



(A) (B)

Figure 8: Constant volume explosion calculations for $\Phi = $ (A) 1 and (B) 3.

Figure 8 contains plots of the time dependence of the mass fractions of a few pertinent species and the temperature. The IPN rapidly dissociates at the beginning of the reaction zone, yielding up

NO_2 which is reduced in two steps, from NO_2 to NO and NO to N_2. On the rich side, this causes a bit of spreading of the temperature rise, and we can that the temperature rise begins to level off before NO reduction comes into play, at which point it climbs again. In mixtures with NO_2 as the primary oxidizer, double cellular structures have been observed on soot foil measurements [19–23]. The effect of the two-stage heat release on the reaction zone, and in turn the detonation structure, is an interesting topic and warrants further study. However, double cellular structure has not been observed in our measurements, and this effect is probably not of great importance to IPN combustion, since there is simply not enough NO_2 for the molecule's size to make it the primary oxidizing species.

There are several possible figures of merit to choose from in such a model to define the induction time. We have chosen to use the time at which the maximum temperature gradient occurs. This figure is multiplied by the previously calculated detonation velocity to obtain the thickness of the induction zone. For the present investigation, this is fit via the method of least squares to a constant multiple of the cell size. A comparison of the correlated calculation and the measured cell widths is located in Fig. 9. The constant of proportionality is 1600. We typically find [24] the detonation cell size to be between 10 and 100 times the reaction zone thickness, so it is clear that our mechanism is dramatically overpredicting the speed of the heat release. This was not unexpected, as it can be seen in Fig. 6 that computed reaction times at high temperature are much lower than were observed in the shock tube. Again, this mechanism is very much a work in progress.

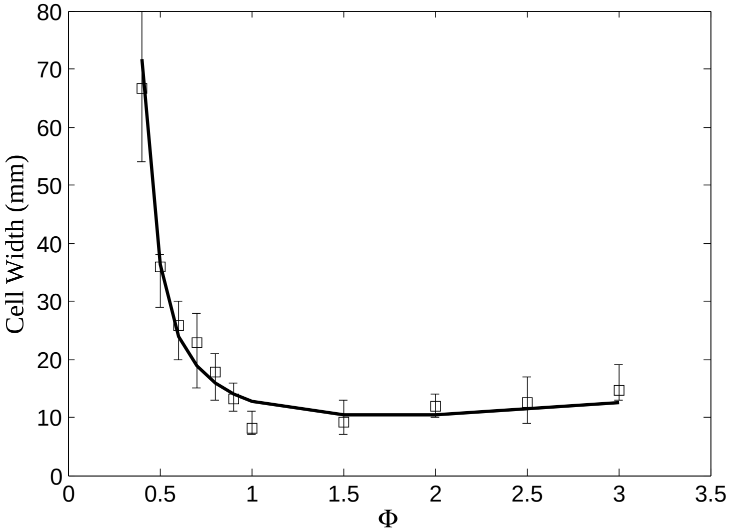


Figure 9: Comparison of correlated reaction zone thickness from constant volume explosion calculation and measured cell size.

4 Conclusions

We have made progress toward an understanding of the behavior of isopropyl nitrate under detonation conditions. Detonation cell widths have been measured for previously uncharacterized mixtures of IPN and air. The detonation velocity and cell size was measured as a function of both equivalence ratio and initial pressure. The detonation velocities were found to be in very good agreement with those predicted by thermochemical calculation. For the sole case in which comparison was possible, the cell width compared well with what was previously reported in the literature.

The results of the chemical kinetic model are encouraging, but the model is still under development. The comparison between the modeling and experimental cell widths shows that the equivalence ratio trends are qualitatively correct, but the prediction of short ignition delay times in the shock tube needs to be investigated further.

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Table 1: List of shots performed in IPN series

Shot	Mixture	Φ	P (kPa)	T (°C)	U_{12} (m/s)	U_{23} (m/s)	U_{CJ} (m/s)	Average Cell Width (mm)	Minimum Cell Width (mm)	Maximum Cell Width (mm)	Notes
1936	IPN-Air	1	20	23			1768				No detonation
1937	IPN-Air	1	20	23	1012.2	849.7	1768				No detonation
1943	IPN-Air	1	40	25	1737.9	1736.0	1842.3				soot foil slightly crumpled after shot
1944	IPN-Air	1	30	26	1820.9	1772.5	1836.0	30.5	23	36	
1945	IPN-Oxygen	1	50	80	2316.5	2311.7	2244				soot foil ruined by water
1946	IPN-Oxygen	1	50	100	2315.4	2310.3	2244				soot foil ruined by water
1947	IPN-Air	1	60	100	1831.8	1815.9	1848.1				much water damage to foil, but usable cells are present
1948	IPN-Air	1	80	97	1837.3	1837.5	1883.7				soot foil ruined by water
1949	IPN-Air	1	100	131	1867.3	1859.6	1853.9				soot foil ruined by water
1950	IPN-Air	1	40	26	1820.9	1819.4	1842.3	23.7	15	30	
1951	IPN-Oxygen	1.5	15	72	2279.0	2263.7	2298.2				
1952	IPN-Oxygen	1.75	15	57	2334.2	2306.0	2328.5				
1953	IPN-Air	1	60	84	1828.2	1815.9	1848.1	15.7	12	20	poor contrast on soot foil
1954	IPN-Air	1	80	77			1853.5				Driver injection failed, DDT in tube downstream of P3. Replaced low or empty acetylene bottle after shot
1956	IPN-Air	1	80	85	1824.5	1812.3	1852.8	11.3	9	13	poor contrast on soot foil
1957	IPN-Air	1	100	76	1869.3	1869.0	1857.7	8.2	7	11	soot foil still not the greatest, contrast getting better though
1958	IPN-Air	0.9	100	113	1811.9	1808.8	1829.4	13.2	11	16	soot foils getting better, still need improvement
1959	IPN-Air	0.8	100	99	1776.7	1772.5	1793.9	17.8	13	21	
1960	IPN-Air	0.7	100	101		1719.9	1751.2				DDT between P1 and P2, mixture pressurized by shock prior to detonation
1961	IPN-Air	0.7	100	104	1739.5	1736.0	1750.9	22.75	15	28	
1962	IPN-Air	1	20	92	1785.4	1767.4	1819.1	32.6	22	43	

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Table 1 – Continued from previous page

Shot	Mixture	Φ	P (kPa)	T (°C)	U_{12} (m/s)	U_{23} (m/s)	U_{CJ} (m/s)	Average Cell Width (mm)	Minimum Cell Width (mm)	Maximum Cell Width (mm)	Notes
1963	IPN-Air	1	10	101	1898.3	1814.1	1802.8	61.08	45	75	
1965	IPN-Air	2	100	112	1963.5	1959.8	1979.3	11.8	10	14	
1966	IPN-Air	0.6	100	108			1695.3				Misfire occured during injection. Flash arrestors cycled. No data from das.
2029	IPN-Air	0.6	100	103	1692.9	1687.0	1695.3	25.7	20	30	
2030	”IPN-Air”	0.5	100	103	1616.6	1615.0	1621.3	36.0	29	38	
2031	”IPN-Air”	1.5	100	104	1932.4	1931.2	1942.8	9.2	7	13	
2032	”IPN-Air”	2.5	100	101	1953.0	1978.7	1995.0	12.5	9	17	
2033	”IPN-Air”	3.0	100	105	1989.1	1982.9	2001.3	14.7	13	19	
2034	”IPN-Air”	0.4	100	99	1504.9	1498.8	1522.7	66.7	54	80	
2035	”IPN-Air”	0.3	100	101	1399.1	1375.4					Poor soot foil, $\lambda \approx 160 - 180$ mm