Explosive properties of energetic systems: application to technological hazards and industrial safety

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The level of understanding and the measures taken in chemical industry with regard to design and engineering aspects of the safe handling of hazardous materials and chemical reactions have been largely improved since the occurrence of major technological accidents like Bhopal, Seveso, Flixborough… Some accidents, including fire, explosion, emission of flammable or toxic substances, have severe consequences on the environment ; they are sometimes irreversible: fatalities, personal injuries and poisoning, destruction of plants or residential zones, air, soil and water pollution, damages to animals and cultural resources. In spite of a demand for higher standards of safety and since risk zero does not exist and human errors will never be eliminated completely, a target level of risk has to be set: inherent safer designs or methods of operation have to be installed, not only by controlling hazards through more equipment protection but also by trying to avoid them or at least prevent minor incidents from becoming major accidents. Such a demand of a lowest risk applies to chemical industry as well as to any kind of industrial (oil, aerospace, military, nuclear…) activities.

One means to ensure more safety and avoid accidents is to develop our knowledge on the explosive properties of energetic systems and on the mechanism of explosive reactions. The area addressed in this paper covers a far from exhaustive research, with the aim of a better understanding of chemistry in the explosion of hazardous chemicals and reactions. This research has been mostly carried out, since almost 30 years, at L.C.S.R., a laboratory belonging to C.N.R.S., with the fruitful cooperation of many scientists and students from France and abroad, with the financial support of a number of industries, governmental and regional organizations, and in the framework of international cooperation with several universities: among them, McGill and Sherbrooke Universities, with a continuous program running over the last 15 years on near-limit detonations.

To help industry to prevent explosions and mitigate the consequences, should they occur, our research effort has been concentrated in two main directions closely linked: shock tube chemical kinetics and initiation/ propagation of flames and detonations, in various energetic (mostly gaseous) mixtures, with a double aim of:

- first, finding the reaction mechanism in a high temperature and pressure range corresponding to an eventual explosion, that is obtaining experimental kinetic data of pyrolysis and/or oxidation reactions, half-life times, rate constants, ignition delays… and comparing them with data issued from a detailed kinetic scheme,
- second, determining the conditions of the initiation and propagation of flames and detonations, of transition from flame to detonation, and measuring flammability and detonability limits, with the aim of pointing out the role of chemical kinetics on the sensitivity of (mostly gaseous) explosives.

Methodology

A set of experimental facilities are at disposal to study either the kinetics of reaction and the ignition delays at high temperature and pressure, either the initiation and propagation of shock waves, flames or detonations. They mainly consist in an array of shock tubes of different size, made of stainless steel or Pyrex glass and equipped with various diagnostics: piezo-electric gages, UV, visible or IR emission and absorption spectroscopy, far UV Atomic Resonance Absorption Spectroscopy, laser schlieren, high speed video camera… One shock tube is adapted to the study of corrosive compounds, others are conceived for being used at high pressures up to 7 MPa, or at initial temperatures up to 150°C for low vapor pressure compounds to be studied.

The main advantage of using a shock tube for high temperature kinetic studies is that the heating occurs almost instantly without any wall effect. The fast reaction can thus be followed at a constant temperature and pressure during a lapse of time exceeding a few hundred µsec, long enough to allow the chemical species to react. The wide range of shock temperatures (500-5000 K) and pressures (a few hundred Pa to several MPa) covers most of the initial conditions encountered in the kinetics of explosions and reactive systems. A large variety of diagnostics well-adapted to the fast evolution of the reaction can be easily coupled to a shock tube and to extremely rapid data processors, leading to an easy exploitation of experimental results.

An original system consisting of a shock tube coupled to a combustion chamber has been built for the determination of ignition limits of an explosive mixture submitted to a hot gas jet. In the same shock tube coupled to a Pyrex glass tube filled with a bubbly liquid, the reflected shock wave can pressurize the liquid and lead to a sequence of contraction and expansion of a single reactive or non-reactive bubble. Flame speeds and flammability limits are determined in a spherical bomb or in a tube via spark ignition. Another Pyrex glass tube equipped with repeated obstacles serves to study the role of chemistry on propagation and acceleration of flames.

Direct initiation of detonation was either obtained in a detonation tube by an electric spark (L.C.S.R.) or in a shock tube via the primary detonation of a higher sensitive mixture in the driver section (McGill and Sherbrooke Universities) or via the bursting of the diaphragm in the shock tube (L.C.S.R.). A large variety of tubes, the diameter of which varies from 0.5 to 80 mm, offers the possibility of studying very sensitive to less sensitive compounds or mixtures (L.C.S.R.), whereas at McGill a loop of connected detonation tubes of decreasing diameters has been specially built for the study of the transmission of near-limit detonations, the extinction or the re-initiation of a detonation after being damped out by a porous wall. Record of mean velocities along the test tube comes usually from piezoelectric transducers signals (or in some cases from thermal or ion gages signals), whereas local velocities, continuously varying in case of highly unstable propagation, are measured via a coaxial microwave Doppler interferometer, from the Doppler-shifted frequency reflected from the moving ionized reaction zone (McGill and Sherbrooke Universities). Inner wall sections of the detonation or shock tube, covered with soot, enables us to record the triple point trajectories and deduce the characteristic size of detonation cells.

Examples of industrial safety studies carried out at CNRS Orleans and in the framework of cooperation

In the manufacture of chlorine by the electrolysis process, nitrogen trichloride NCl_3 is a by-product easily formed by reaction of chlorine with nitrogen compounds. Subsequent extraction of NCl_3 from liquid chlorine is the cause of many accidents in chlorine plants. This is due to the unstable nature of NCl_3, a highly endothermic compound. It is also a hazard in water chlorination process and in wastewater treatment when chlorine or bleach is reacted with nitrogen containing organic or ammonium ions.

When chlorine is happened to be intentionally or accidentally into contact with an organic vapor (1,4-dioxane for example) in an enclosed surrounding, the explosion hazard is important. Such an explosion can be accompanied with an overpressure leading to the vessel rupture. Considering the various process situations where the formation of NCl_3 or the contact of an organic solvent with Cl_2 is a hazard, the French “Rhône-Poulenc” chemical company asked for a scientific support to risk assessment in chlorine production and use.

Another chlorinated compound, chlorine dioxide ClO_2, used as a bleaching agent, is known as to be a highly unstable compound in the gaseous state, as it readily decomposes in an explosive manner, even at low initial pressures. Owing to the simplicity of the molecule, a detailed study covering many aspects of ClO_2 explosive behavior was done under contract with the Ministry of Defense and served as a model for fundamental knowledge of a simple reactive system.

There has been a constant interest in liquid propellants such as hydrazine and its methyl (MMH and UDMH) derivatives, for spacecraft and rocket use, thanks to the high potential of energy contained in their molecules. MMH and UDMH are generally associated with N_2O_4 in storable energy engines ; MMH, nowadays used for the space shuttles, for the European launcher Ariane 5, and for numerous satellites has progressively replaced UDMH, the fuel still used in Ariane 4. Hydrazine primary serves as a monopropellant for satellites for its exothermic decomposition to provide thurst for maneuvering, and second, as a fuel in the auxiliary power units of the Space Shuttle Orbiter or in the Attitude Control System of Ariane 5. Unfortunately, the instability that makes these compounds ideal for aerospace applications also makes them very hazardous. They are indeed endothermic compounds, thus able to decompose either gently or violently ; they react with oxygen, even at room temperatures, often violently, and give hypergolic mixtures with N_2O_4. Although incidents have been rare, occasional explosions have caused severe structural damage. A thorough knowledge of their explosive properties are essential for a safe handling of hydrazine systems. Despite numerous studies over the past decades, a lack of data on the kinetics of decomposition and oxidation of these compounds in the gas phase, as well as on their detonation hazard, has required an extended study, mostly carried out at CNRS, financially supported by “CNES”, “Matra Space”, the Ministry of Defense, also by “NASA-Lockheed - WSTF”, with McGill University.

Moreover, in the framework of the stability of propellants and the sensitization of liquid explosives, interest has been brought on the problem of ignition of explosive gas bubbles trapped in a liquid and rapidly compressed. An explosion of gas bubbles trapped in liquid hydrazine might occur in the hydrazine systems, in case of a partial catalytic decomposition of hydrazine during the waiting period prior to firing of the European Ariane 5 rocket at Kourou base. This explosion could be due to a waterhammer effect induced by the latch valve opening in the Attitude Control System. To help “CNES” to build an explosion model, not only experiments on rapidly compressed bubbly liquid were necessary, but also a detailed and comprehensive re-examination of the decomposition mechanism of gaseous N_2H_4 in presence of N_2, H_2, NH_3, eventually present in the gas bubbles.

Similarly, nitromethane, a relatively stable liquid explosive, can be sensitized with the introduction of gas bubbles in the liquid. Although nitromethane frequently serves as a model for liquid nitro-propellants detonation and is the object of countless studies, the gas phase reactions of decomposition or oxidation at high temperature and pressure have been scarcely investigated. However, in case of a rapid compression impinging on bubbly liquid nitromethane, a detonation may be initiated, the mechanism of which implies the kinetic modeling of the gas phase reactions occurring inside the bubble and the determination of ignition delays.

Industrial safety also concerns the natural gas producers and suppliers, since natural gas is more and more used as an energetic source in various areas. Its explosive properties strongly depend on its composition, then on the country where it comes from. For example, Russian gas, mainly constituted of methane, has a detonation sensitivity lower that of Middle East gas, that is enriched with heavier hydrocarbons. As risk assessment is usually based on methane behavior, "Gaz De France" company initiated a systematic study of ignition delays and of flame propagation in presence of repeated obstacles, in {CH_4/air} mixtures doped with different additives, in order to look at the influence of chemistry on ignition and flame acceleration.

Although the H_2/air system is rather well known, the ignition conditions by a hot gas jet is of great interest for nuclear reactor safety. Indeed a failure in the reactor core cooling, as it occurred in the Tchernobyl nuclear accident, can generate in the vicinity a combustible medium of H_2/air/steam. This mixture can be ignited by the hot gas jet emerging from a leak and containing a high H_2 content. "Electricité De France'' that runs all nuclear power plants in France is mostly concerned in such a technological hazard linked to hydrogen explosion.

This contract with EDF has been the logical consequence of my intense research work since 1984, in the framework of French/Canadian cooperation, on near-limit propagation of lean H_2/air detonations, at McGill University, and punctually at SNLA. After the accident of TMI-2, the objective was nuclear plant safety. Then our interest was to arrive at some meaningful correlation for detonation limits in various fuel/air mixtures, to examine the role of transverse waves on detonation stability and to identify the parameters that govern the near-limit unstable phenomenon appearing beyond single headed spin. At McGill, then at Sherbrooke Universities, the galloping regime, highly detrimental to industrial equipment, should it occurs, has been carefully studied.

Beside numerous studies carried out with French and foreign colleagues, in a rather far past or on subjects not connected to safety, beside the continuous cooperation with McGill and Sherbrooke Universities, a number of recent studies concerning industrial safety has been the fruitful outcome of cooperation with:
- a major French organization, C.E.A.- D.A.M. le Ripault, for the reactivity of solid TATB and HMX explosives,
- the University of Nancy, for the influence of halons on methane auto-ignition,
- The I.S.L. of Saint-Louis, for a study of the explosion hazard in the unburnt gas of a Ram Accelerator,
- the University of Duisburg (Germany), for the high-temperature reaction kinetics of silicon tetrachloride,
- the HEDRIC (ex IVTAN) in Moscow (Russia), for the modeling of detonation cell size from the reaction mechanism and the thermodynamic properties of the given mixture, using the model of Vasiliev and Nikolaev,
- the University of Galway (Ireland), for the pyrolysis and oxidation of dimethyl ether (DME), an attractive diesel-fuel option due to its high cetane number, low boiling point and high oxygen content,
- the University of El Jadida (Morocco), for similar studies on methyl- and ethylformate, two volatile organic compounds mainly used in manufacturing perfumes and flavoring.

High-temperature kinetic studies of decomposition or oxidation

For high-temperature kinetic studies of decomposition or oxidation, the reactive mixture is submitted to a reflected shock wave: the main reactant concentration is generally followed via an absorption technique at a typical wavelength close to the shock tube end, and the shock arrival detected by a piezoelectric detector. Concentration profiles, half-life times, reaction rates and ignition delays are obtained in a certain range of shock temperatures and pressures. From the logarithmic evolution of reaction rate constant and of half-life time with inverse shock temperature, the activation energy and reaction order are deduced ; the ignition delays τ_i of decomposition or oxidation can be formulated as $\tau_i = K\ [\text{Fuel}]^m\ [\text{Oxidant}]^n\ [\text{Diluent}]^p \exp(E/RT)$ by using a least-squares multi-regression. This expression is useful to estimate the explosion hazard of a given system, and especially its sensitivity to detonation. Simultaneously with experiments, a detailed reaction model serves, in addition to predict the kinetic parameters, to calculate the sharp increase of temperature, pressure and radical concentration corresponding to ignition. It also allows a comparison between computed and experimental τ_i.

The thermal decomposition of hydrazine diluted with more than 98% N_2 or N_2/He has been carried out behind reflected shock waves between 0.2 to 1.3 MPa, 1100 to 1400 K. For $P < 0.5$ MPa, the decomposition reaction belongs to the fall-off zone. A partial substitution of He in N_2H_4/N_2 mixtures has shown that the overall rate constant and the fall-off depend on the nature of diluent. As the initiation step is found to govern the mechanism, it is, as found for the overall reaction, a unimolecular one. A detailed kinetic model, built according to all experimental data, has been proposed for pressures higher than 0.5 MPa. It involves the rate constant k_∞ value, a unimolecular initiation step, 48 elementary reactions and 11 chemical species, and takes into account the diluent effect on the rate constant. Other additives (NH_3, H_2), eventually present in the gas bubbles as products of a partial N_2H_4 catalytic decomposition, have been examined in terms of their promoting or inhibiting effect on the chemical reaction. Similar kinetic studies have been systematically done for most explosive systems studied.

The determination of the ignition delay of MMH decomposition τ_i, defined as the time interval between the arrival of the reflected shock wave and the beginning of the reactant absorption signal, has been the object of a large number of studies. A full kinetic model (99 elementary reactions and 39 species) and a reaction scheme, reduced with the help of sensitivity analyses, have been built for MMH decomposition to fit the experimental decomposition profiles of largely diluted mixtures. They serve to evaluate the MMH detonation sensitivity.

The high-temperature reaction of MMH/O_2/Ar (or UDMH or NM/O_2/Ar) mixtures is, for certain initial conditions, a two-phase process, that consists first of a rapid decomposition of the endothermic fuel, followed by the oxidation of the decomposition products. The ignition delay τ_i for the oxidation is defined as the time interval between the reflected shock arrival and the beginning of a sharp emission signal due to the exothermic oxidation reaction. A correlation is found between τ_i, T, and concentrations of fuel, oxygen and argon. A 300 reaction-model based on MMH decomposition and on the oxidation of decomposition products, developed for comparing experimental and theoretical ignition delays, has also been validated for MMH/O_2/H_2/Ar and H_2/O_2/Ar mixtures. Contrary to this previous case, the 1,4-dioxane/Cl_2 reaction is not a two-step process. Data analysis of ignition delays and half-life times shows that, during the auto-ignition, chlorine plays a promoting role in dioxane decomposition, especially at the beginning of the reaction. The kinetic mechanism of dioxane/Cl_2 reaction is found to be a complex one with branching reactions in which chlorine atoms might have a strong influence.

Auto-ignition limits, flame propagation, flammability and ignition limits

Gaseous NCl_3 is a hazard because of its very peculiar explosive properties: it undergoes auto-ignition very easily, at extremely low initial pressure (some Pa or kPa) and concentration (less than 3 mol% NCl_3). The auto-ignition limits were determined at ambient temperature in a spherical vessel and in horizontal tubes of different diameters by lowering the initial pressure of different {NCl_3/Cl_2/N_2 or Ar} mixtures. A quasi-isothermal flame front was found to propagate, strictly sustained by a radical diffusion mechanism.

Even highly diluted, MMH reacts immediately when nitrogen tetroxide (N_2O_4/NO_2) comes into contact: it is due to the very low energy of the reaction of MMH with NO_2, acting as a monovalent radical. A white fog is first formed, due to MMH nitrate, which may lead to an explosive reaction, depending on initial conditions. The addition of NO_2 induces an even more violent reaction, and shows how hazardous these hypergolic mixtures are.

Outside the auto-ignition area, endothermic compounds (like HN_3, N_3Cl, N_3Br, ClO_2, N_2H_4, MMH or UDMH) or fuel/oxidant mixtures being potentially explosive slowly decompose or react. Submitted to an electrical spark or to any shock, they are able to explode and lead to the formation of a flame. From NCl_3 fundamental velocities and flame temperatures, a low activation energy of the explosive decomposition (≈ 25 kJ mol^{-1}) has been deduced, showing with all other results the very unstable and peculiar behavior of gaseous nitrogen trichloride Experiments were performed in a spherical vessel with spark central ignition to determine the flammability limits of NCl_3 diluted with nitrogen. It follows that NCl_3 is a real hazard for chlorine industry, as flammability limits correspond to NCl_3 molar fractions as low as 0.005 or to partial pressures lower than 5 Pa.

An alternative way is to calculate the flammability limits of a given mixture by using the additive rules of Le Châtelier and the method proposed by Jones for complex industrial fuels/O_2/N_2 mixtures. Such a calculation has been done to estimate the flammability hazard due to the presence of unburnt gas (H_2, CH_4, CO) in the exhaust mixture emerging from the ram stages of a ISL Ram Accelerator. The exhaust gas/air mixture was found to be flammable, and thus could lead to an explosion on contact with the hot surface of the catcher heated by the impact of the projectile on the metallic blocks. A simple and cheap means of avoiding explosion has been proposed, that is replacing air by nitrogen in the decelerator section.

The study of the ignition, subsequent combustion and ignition limits of a {hydrogen/air + diluent} mixture by means of a hot transient gas jet, at initial temperature ranging from 750 to 3000 K, has required the construction of an original test facility, able to be heated up to 403 K. It consisted of a shock tube connected at its downstream end to a combustion chamber via an injector. The aim was to produce an unsteady subsonic hot gas jet able to induce a flame in a cold {H_2/air + CO_2} or initially heated {H_2/air + CO_2 or H_2O vapor} mixture confined in the combustion chamber. The ignition limits of such mixtures were determined and compared to the classical flammability limits due to spark ignition. Among all parameters examined, the initial jet temperature is the most important. But the ignition process is not a purely thermal one: the nature and the composition of the gas (essentially H_2 and Ar) in the hot jet also play an important role in the ignition mechanism, due to the presence of atomic hydrogen at reflected shock temperature. The ignition areas of {H_2/air}mixtures diluted with CO_2, at 100 kPa and 403 K, are more extensive than with steam. Compared to the classical flammability limits in the same range of initial temperature, the ignition area in case of steam dilution is noticeably reduced. These results clearly show that the ignition phenomenon is influenced, not only by gas dynamic effects different in both types of ignition, but also by the chemical effect due to a stronger efficiency of CO_2 acting as a collision partner.

Transmission of a compression wave to a bubbly liquid

To analyze the conditions of transmission of a compression wave in a bubbly liquid, a reflected shock wave issued from a shock tube was directly transmitted to a liquid contained in a Pyrex cylindrical tube in which a single macro-bubble filled with a reactive (or non-reactive) gas was attached to the upper wall. As it was too dangerous to work on a reactive bubble in liquid N_2H_4, water was used instead of N_2H_4, with a bubble of a reactive {$H_2/O_2/Ar$ or $C_2H_4/O_2/N_2$ or Ar} or non-reactive {H_2/Ar or C_2H_4/N_2 or Ar} mixture. Results could be easily extrapolated, due to similar properties. The pressure variation in the liquid close to the bubble could be followed via piezoelectric transducers and the sequence of the compression and expansion phases of the bubble visualized thanks to a high-speed video camera. A unique complete cycle is observed with the gas-liquid interface integrity kept during the compression phase, then Rayleigh-Taylor instabilities appear at the interface during the bubble expansion. Bubble ignition is detected by comparing the pressure gradients and bubble deformations occurring in both cases of a combustible bubble and of an inert one. The eventual ignition of the reactive bubble occurs during the first cycle and is closely linked to the bubble initial size. With the assumption of an adiabatic compression, the conditions of ignition of a given mixture were found experimentally.

Acceleration of flames with repeated obstacles

An extensive work has been done on this important safety problem of flame acceleration in presence of repeated obstacles and the associated physical mechanism described. Chemistry appears generally in the form of an overall reaction equation associated to its enthalpy. Our experimental configuration consisted in a Pyrex tube separated from an expansion reservoir at its downstream end via a Mylar diaphragm and equipped with a series of piezoelectric transducers and a fast video camera (6000 images/s) for flame visualization. An array of moveable obstacles could be installed inside the tube. Besides the influence of the obstacles spacing and position in the tube, a special interest was brought on the role of chemical kinetics on turbulent flame propagation and acceleration: it is why two premixed flames of stoichiometric CH_4/air and C_2H_6/air, with similar velocities and flame parameters, but with different reaction rates were chosen. In a smooth tube, both flames propagate at a similar velocity whereas, in presence of obstacles, more rapid accelerations are observed with ethane. However, transition to detonation was never observed, in the range of low initial pressure (<33 kPa) studied.

Transition from a shock wave to a stable, self-sustained detonation

If an explosive mixture, at a given composition and fixed initial pressure P_1, is confined in a shock tube and submitted to the incident shock wave, it is rapidly heated and pressurized to incident shock temperature T_2 and pressure P_2, depending on shock strength. A detonation can be initiated only if the pressure ratio P_4/P_1 across the diaphragm is high enough, that is larger than the critical ratio $(P_4/P_1)_c$ necessary to induce a coupling between the shock front and the reaction zone. To this critical ratio experimentally found from wave velocity versus P_4/P_1, there are corresponding critical shock pressure P_c and temperature T_c for the transition to detonation. It is crucial to take into account these critical values for a safe handling of the given mixtures.

It is to note that a stable, self-sustained detonation only occurs in a restricted range of initial pressure P_1. With dioxane/chlorine mixtures, for example, the mixture is not sufficiently energetic at low P_1 (< 2;7 kPa) to allow the coupling, with a moderate P_4 value. At higher P_1 (> 6.8 kPa), the shock intensity is too weak to initiate a detonation behind the incident shock. However, a detonation may be initiated, behind the reflected shock, in the mixture pre-heated and pre-compressed by the incident shock. It is a real hazard: it occurred once and provoked the shock tube burst. Great care must also be taken in case of a large P_4/P_1 ratio: tiny detonation cells and overdriven velocities may be observed at initial pressures below the detonation limit pressure. It occurred once with chlorine dioxide. It is obvious that a too strong initiation energy leads to an abnormal behavior of the mixture, and provides a real hazard due to the large excess of energy added to the chemical energy release.

It is why the critical ratio $(P_4/P_1)_c$ has to be imperatively measured for each explosive mixture studied. Just beyond this sharp value, an overdriven detonation takes place, with a velocity much higher than the C-J theoretical velocity and a cell size abnormally small. This can be the cause of high structural damages, should an explosion is initiated. For much larger than $(P_4/P_1)_c$ values at a constant initial pressure, the detonation wave tends to become a stable and self-sustained wave with a quasi-constant velocity, just lower than the V_{CJ} value.

Sensibility to detonation

Given an adequate pressure ratio across the shock tube diaphragm, the study of a stable, self-sustained detonation is carried out in a certain range of mixture composition and initial pressure. The aim, linked to safety, is to determine the sensibility to detonation of the given mixture. The detonation velocity measurement, although useful, must be accompanied, at least, by a cellular structure analysis. Cell size λ is indeed the fundamental (but not the unique) detonation parameter that permits to rapidly compare the sensitivity of different explosive mixtures. As far as the cellular structure is more or less regular, cell size can be measured, using the soot foil technique. It can also be deduced from the induction distance Δ calculated, using the ZND model, from the experimental ignition delay τ_i, according to the relation: $\Delta = \tau_i (V_{CJ} - v)$, provided that the proportionality factor A in the relation $\lambda = A\,\Delta$ is known for the given mixture. An alternative way is, knowing the detailed kinetic mechanism of the explosive reaction, calculate the ignition delay and deduce the detonation cell size. Study of detonation sensitivity was carried out systematically with all mixtures considered. Below are two examples.

Detonation cellular structure of pure hydrazine vapor was studied in a 150 mm heated tube between 0.67 and 120 kPa initial pressure and initial temperatures between 308 and 393 K. Cells were found to be very regular and correlate very well with the induction distance Δ, if an empirical value of 29 for A is used in the relation $\lambda = A\,\Delta$. The limited experiments on critical tube diameters for propagation of a detonation into an unconfined space showed that the 13λ relationship holds reasonably well. The detonation sensitivity of N_2H_4 vapor is closed to that of C_3H_8/O_2 mixtures but much higher than that of MMH. Gas-phase detonations may be responsible of violent explosions that occasionally cause severe damage to hydrazine systems.

A detonation study in lean, stoichiometric or rich 1,4-dioxane/Cl_2 mixtures, undiluted or diluted with Ar, has been carried out in the same Pyrex shock tube as for ignition delay measurements. The cellular structure is generally irregular and filled with microstructures and no constant A value exists between λ and Δ. Detonation sensitivity of stoichiometric dioxane/Cl_2/50% Ar mixtures lies between that of methane/oxygen and that of hydrogen/oxygen mixtures. In spite of cell size irregularity, the presence of cells or spin on the soot foil confirms that dioxane/Cl_2 mixtures are able to detonate and that a detonation hazard does exist with these mixtures.

Detonability limits and detonation stability

To arrive at some meaningful correlation for limits based on both velocity deficits and fluctuations, an extensive detonation study of lean, stoichiometric and rich fuel/air mixtures was carried out, at McGill University, in a continuous loop of five tubes of decreasing diameter. In order to point out the role of confinement and therefore that of transverse waves on the propagation and the stability of detonations, an acoustic damping section, consisting in an absorbing material lined on the inside wall of a short tube section at the beginning of each tube of the loop, serves to get a well-defined initial condition, that is a decoupled shock-flame complex propagating at half C-J velocity. The ability of this complex to transit to detonation, according to the sensitivity of the considered mixture and to the ratio λ/d of cell size over tube diameter, was the base of a detailed analysis of failure, of galloping detonation-like phenomenon and of stable self-sustained detonation.

A recent study was to explore further the highly unstable nature of the detonating regime beyond single headed spin, characterized by very large longitudinal velocity fluctuations over relatively long periods, with a continuous monitoring of the local wave velocity along the entire tube length ($\approx$ 25 m). To do this, a novel microwave Doppler interferometer, based on a single coaxial mode, has been developed at McGill University, as well as a computer software providing reliable local velocity data with high spatial resolution. The equipment has been recently transferred at Sherbrooke University. Tested mixtures of stoichiometric hydrocarbons (C_2H_2, C_2H_4, C_2H_6, C_3H_8) with O_2, air, N_2O have been characterized by, at least, four distinct propagation regimes: the classical C-J detonation, the unstable stuttering and galloping modes, and the fast flame mode. For each $C_3H_8/5O_2$ mixture, diluted or not with Ar or He, the limiting initial pressures for each mode were determined. The galloping mode could not be obtained at dilutions equal to or above 70% Ar and 60% He. Arguments based on computed induction times were used to explain the effect of dilution and diluent on the onset of the galloping regime, but they could not explain the specific amplitude and period of galloping detonations. A recent theoretical work based on Eckett's model has been directed towards the stability analysis of this phenomenon, for a better understanding of the intrinsic properties that govern galloping detonation behavior.

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