Auto-ignition delay times and detonation cell size
of hydrogen-nitrous oxide-argon mixtures

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1   Introduction

Silicon containing gaseous compounds, such as silane or chlorosilane, are of large interest in some kinds of industries such as semiconductor and ceramic material production since they can be used in order to produce SiC, Si_3N_4 or SiO_2 powders [1]. Using thermal or plasma enhanced chemical vapour deposition processes, silicon dioxide solid films can be formed as protective layers and electrical insulators [2]. As a consequence of the necessary conditions for the thermal processes, that are close to those used for low pressure combustion reactions, a risk of ignition and explosion has not to be excluded [2]. Among all silicon based compounds, silane seems to be the most hazardous. Indeed, it presents a very wide flammability domain, a very large flame temperature range, a pyrophoric behaviour for concentration above 4.5 mol % in air, and very high pressure rise rate and burning velocity [3].

Although Hirano [4] reports an explosion that has been attributed to silane-nitrous oxide mixtures, very few papers deal with explosives properties of this system. However, Horiguchi et al. [5] have shown that, at room temperature and atmospheric pressure, these mixtures are stable but present a wide flammability domain since it ranges from 1.90 to 87.1 mol % SiH_4. An important behaviour of silane is its decomposition mechanism. First, it must be noticed that this decomposition reaction is fast for temperatures as low as 1200 K, whereas the one of nitrous oxide remains slow at this temperature [6]. Moreover, many kinetic studies have shown that silane decomposition leads to the release of molecular hydrogen [7]. It follows that the H_2-N_2O chemistry might play an important role in the SiH_4-N_2O system.

Some studies have been carried out on induction delay times of these mixtures [8], essentially at low pressure. Besides, the detonation sensitivity of H_2-N_2O-(N_2) mixtures with respect to equivalence ratio Φ, to diluent percentage and to initial pressure has been investigated [8-9]. As part of this study, several available kinetic models have been tested. The so-called "modified" Miller and Bowman model has been reported as the best one chosen to model induction times of H_2-N_2O-Diluent mixtures [8].

The aim of the present study is to investigate the high pressure behaviour of H_2-N_2O-Ar mixtures via a characteristic time of reaction (τ_c) defined thanks to the OH radicals UV emission. Besides, using the "modified" Miller and Bowman model and an OH* sub-mechanism, the experimental data have been modelled. Finally, using the resulting mechanism and detonation cell width (or size) data previously determined at Caltech [8-9], an attempt has been made to correlate the cell size-induction distance ratio with initial conditions.

2   Experimental set-up

In order to avoid possible systematic errors due to gas impurity, high-purity gases supplied by Air Liquide have been used: up to 99.999 % for argon (diluent), helium (driver gas) and hydrogen, and up to 99.998 % for nitrous oxide. Each mixture has been prepared in a 50-L stainless steel mixing tank using the partial pressure method. Although N_2O is able to form a flame by itself, since its decomposition, $N_2O+M=N_2+1/2O_2+M$, is

exothermic, it is considered as the oxidant for the equivalence ratio calculation. The stoechiometric equation taken into account is H$_2$+N$_2$O=H$_2$O+N$_2$, so that Φ corresponds to the hydrogen molar fraction to nitrous oxide molar fraction ratio.

   The driver section of the shock tube used in this study is a stainless-steel cylinder of 0.9 m long with external and internal diameters of 141.3 and 128.2 mm, respectively. The low pressure section is a 3.80 m long stainless-steel cylinder which has external and internal diameters of 88.9 and 78.0 mm, respectively [10]. For delay measurements, the working part of the shock tube is equipped with several diagnostic instruments: 4 pressure transducers, a fused silica optical window, located at 10 mm from the end wall, and an UV-sensitive photomultiplier associated with a narrow-band filter centered at 307 nm. The two sections are separated by a double diaphragm and are pumped down prior to experiment.

3   Results and discussion

   Characteristic times of reaction behind reflected shock waves of H$_2$-N$_2$O-Ar mixtures have been measured in the 1300-1860 K temperature range, at 912 ± 70 kPa for mixtures with Φ = 0.5, 1 and 2. They are defined as the time difference between the wave passage and the time corresponding to 50 % of the (A$^2\Sigma^+$-X$^2\Pi$) OH emission peak height. Using the "modified" Miller and Bowman model, the evolution of mixture composition behind the incident shock has been studied. It appears that less than 0.05 mol % of both H$_2$ and N$_2$O reacts after a period of 1 ms. This period being very long compared to the time difference between the incident and reflected shock passages at the measurement point, it can be concluded that the mixture composition is not modified by the incident shock.

Figure 1 presents the characteristic times of reaction obtained for 99 mol % Ar diluted mixtures with Φ = 0.5, 1 and 2, versus the inverse of reflected shock temperature, at reflected shock pressure P$_5$ = 912 kPa. As seen in this graph, τ_c obtained for each Φ cannot be distinguished in the whole temperature range studied. That means that equivalence ratio has no influence on τ_c of H$_2$-N$_2$O-Ar mixtures, at that given pressure.

   In order to model the characteristic times of reaction of H$_2$-N$_2$O-Ar mixtures, the "modified" Miller and Bowman mechanism, associated with thermodynamic data of Konnov [11], has been used. Considering the high dilution of the studied mixtures, the constant volume reactor model was used. As seen in Figure 2, the model overestimates experimental values in the whole temperature range since the difference between numerical and experimental data is as high as 100 %. In order to get a better agreement, a kinetic sub-mechanism including electronically excited OH* radicals [12] has been added to the existing model. Besides, the reaction N$_2$O+H=N$_2$+OH* from Hidaka [13] was included. The resulting model is called "excited" Miller mechanism. Thermodynamic data of the OH* radical has been taken from reference [14]. The numerical results obtained for mixtures of Φ = 0.5 are presented in Figure 2. As it can be seen, the agreement with experimental delays is quite satisfactory. Predictions for mixtures with Φ = 1 and 2 are also good. This permits to conclude that the ground state OH time profile does not coincide with the OH* temporal evolution, as seen in Figure 3. Consequently, the use of excited OH* chemistry is necessary in order to get a satisfactory model of the hydrogen-nitrous oxide-argon mixtures chemistry. With this model, reaction pathways have been analysed at low, medium and high temperature. The time taken into account is the characteristic time of reaction. It appears that the only reaction that leads to a production of OH* radicals is N$_2$O+H=OH*+N$_2$. For a further investigation of this reaction path, the H production rates have been calculated. No significant variations of production rates with equivalence ratios have been noted. A large majority of H radicals is produced via the OH+H$_2$=H$_2$O+H reaction. From this analysis it can be concluded that equivalence ratio variations between 0.5 and 2 have no influence on the OH* formation pathway and thus on τ_c.

   The idealised ZND detonation structure model permits to link the detonation cell size, λ, to the induction distance, Δi, via the A ratio (A = $\lambda/\Delta i$). The induction distance is linked to the auto-ignition delay time defined according to the Zeldovich, Frank-Kamenetsky, Semenov theory of adiabatic explosion. Using the developed kinetic mechanism and the 31 available detonation cell size experiments carried out at Caltech [8-9], the A ratio has been estimated for each experiment. Its mean value, equal to 48.6, with a standard deviation of 28, has been calculated and used to determine theoretical cell widths. However, the comparison with experimental cell size data shows large discrepancies (with a maximum relative error of 500 %). A detonation wave can develop in a

tube if its cell size is less than 3 times the tube diameter. Thus, tube diameters can be adjusted in order to avoid the formation of a detonation. However, a non-accurate prediction of cell size would lead to a high uncertainty in the design of safe industrial equipments. It is why a better way to estimate the A ratio has been investigated. Applying a multiple regression to all A values, an empirical expression has been deduced, giving the A ratio as a function of equivalence ratio, dilution and initial pressure. The obtained equation is the following, with Φ the equivalence ratio, x the mole fraction of diluent, P_1 the mixture initial pressure and $P°$ the standard pressure:

$$A = 47.46 \cdot \Phi^{-0.350} \cdot (1-x)^{0.106} \cdot \left(\frac{P_1}{P°}\right)^{0.695} \tag{1}$$
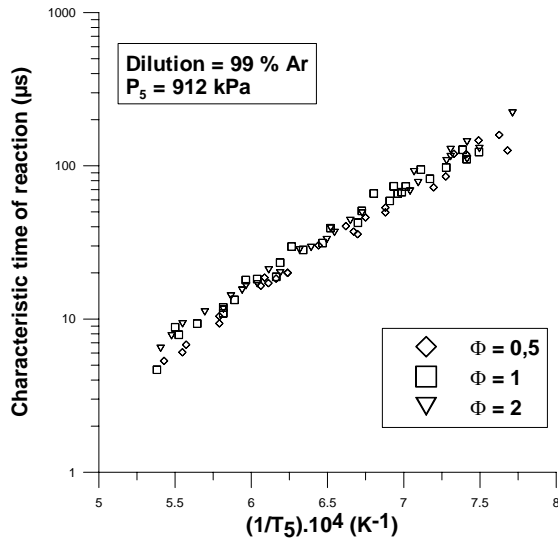

Figure 1: Evolution of experimental characteristic times of reaction of H$_2$-N$_2$O-Ar mixtures versus inverse reflected shock temperature.
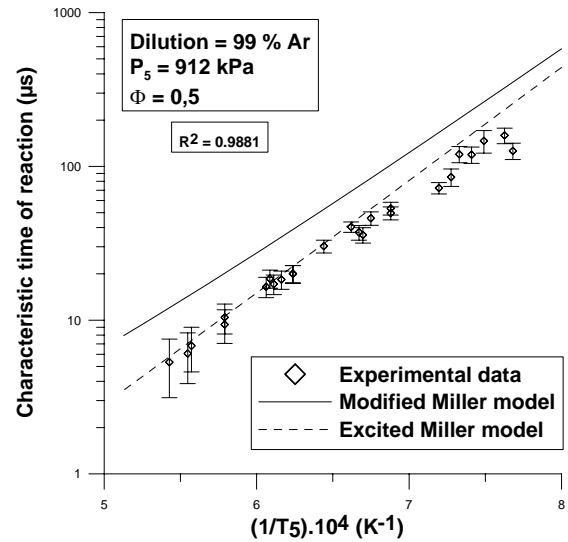

Figure 2: Modelling of H$_2$-N$_2$O-Ar mixtures characteristic times of reaction of versus inverse reflected shock temperature with the "modified" Miller & Bowman and the "excited" Miller models.
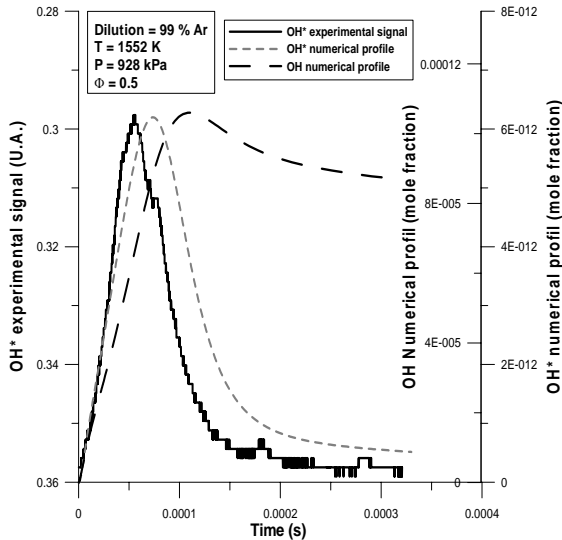

Figure 3: Comparison of OH* experimental signal with OH* and OH simulated profiles for H$_2$-N$_2$O-Ar mixtures.
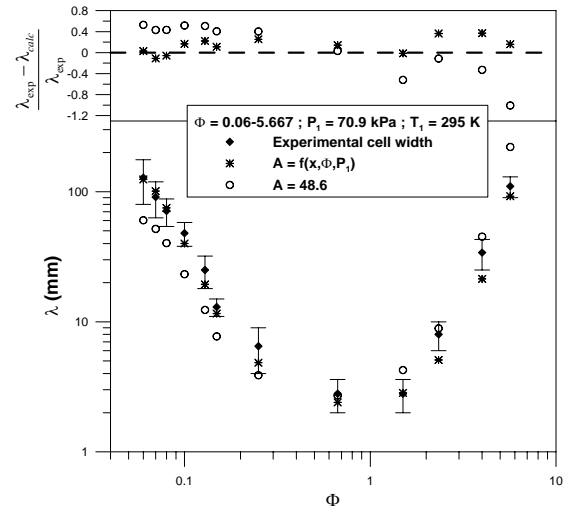

Figure 4: Evolution of experimental, correlated and calculated cell width versus equivalence ratio, for H$_2$-N$_2$O mixtures.

Although the correlation coefficient obtained for the regression is quite low, 0.7614, the mean relative error on calculated detonation cell size is 26 %, with a maximum of 110 %. These percentages give evidence of the improvement brought by the use of the correlated A ratio value since the mean relative error is reduced by a factor of almost 3 and the maximum error by a factor of almost 5. This correlation is valid in equivalence ratio, dilution and initial pressure ranges 0.06-5.667, 0-70 % and 10.1-100 kPa, respectively.

Figure 4 shows the evolution of cell size with respect to equivalence ratio for non diluted H_2-N_2O mixtures, with initial pressure and temperature of 70.9 kPa and 295 K, respectively. Relative errors on predicted cell sizes using equation (1) and A = 48.6 are also presented. It can be seen that for almost all data, the cell width obtained via the empirical equation is closer to the experimental values than the values obtained with an A ratio equal to 48.6. Globally, 77 % of the 31 experimental cell size data are better predicted using the correlated A ratio.

4 Conclusion

Characteristic times of reaction of H_2-N_2O-99 % Ar mixtures have been studied in the 1300-1860 K temperature range and at a pressure of 912 kPa. It has been shown that equivalence ratio varying between 0.5 and 2 has no effect on these times in the whole temperature range.

An accurate modelling of characteristic times of reaction has been developed via the introduction of a sub-mechanism that takes into account the chemistry of OH* radicals, into the "modified" Miller mechanism. Using the resulting "excited" Miller model, both H and OH* radicals reaction pathways has been analysed. It appears that the variation of equivalence ratio between 0.5 and 2 does not modify the OH* formation path and thus has no influence on characteristic times of reactions.

Thanks to this model and to experimental cell size data, the cell size-induction distance ratio has been correlated with respect to equivalence ratio, dilution and initial pressure. This correlation leads to a detonation cell size of H_2-N_2O-(N_2) mixtures with a mean relative error of 26 %.

Although detonation experiments available in the literature cover a wide range of equivalence ratio, dilution and initial pressure, they all have been carried out with N_2 as diluent. Consequently, in order to check the validity of the empirical expression with Ar as diluent, a set of new experiments are to be realised on Ar-diluted mixtures.

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