Pathological Detonations in H_2-Cl_2

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Introduction

Detonations with steady-state velocities in excess of their equilibrium Chapman-Jouguet values are generally referred to as pathological detonations. The existence of such pathological detonations requires a special way in which the exothermic and endothermic elementary kinetic processes proceed toward equilibrium. The possibility of pathological detonations in the H_2-Cl_2 system was first pointed out by Zeldovich [1] in 1941. He pointed out that on the basis of the Nernst chain for the H_2-Cl_2 reaction, two molecules of HCl are produced from H_2 and Cl_2 without a change in radical concentration of H and Cl, i.e. $H+Cl_2 \rightarrow HCl+Cl$, $H_2+Cl \rightarrow HCl+H$. Thus, the reaction $H_2+Cl_2 \rightarrow 2HCl$ can proceed to equilibrium at any concentration of the radicals H and Cl. Since the activation energies for the reactions $H+Cl_2 \rightarrow HCl+Cl$ and $H_2+Cl \rightarrow HCl+H$ are relatively small as compared to the dissociation energy of the Cl_2 itself, the formation of HCl can proceed much faster than the equilibration of Cl_2 molecules. Thus the highly exothermic reaction of HCl formation from $H+Cl_2 \rightarrow HCl+H$ can lead to an overshoot in the energy release which is subsequently absorbed in the endothermic dissociation reaction of Cl_2. The detonation velocity for the H_2-Cl_2 system can therefore be determined by the maximum heat release and not the equilibrium value. Guénoche et al. [2] later carried out a more detailed kinetic study of the ZND structure of H_2-Cl_2 detonations and confirmed the possibility of pathological detonation for H_2-Cl_2 mixtures proposed by Zeldovich.

Satisfactory experimental confirmation of the existence of pathological detonations in H_2-Cl_2 mixtures has not been established. Although Zeldovich and Ratner [1] Knystautas and Riopelle [3] and Akyurtlu [4] all indicated that higher than equilibrium CJ velocities were observed, the results are not sufficiently accurate to permit an unambiguous conclusion of the existence of pathological detonations. For example, in the experiments of Akyurtlu, velocities as high as 50% above the equilibrium CJ value were reported. This was later found to be due to near limit unstable phenomenon. In the study by Knystautas and Riopelle, the tube length was insufficient to ensure steady-state stable propagation. Hence it appears of value to carry out more precise measurements of detonation velocities as well as pressure in the H_2-Cl_2 mixtures to confirm the existence of pathological detonations. Also, the independence of the detonation velocity of H_2-Cl_2 as proposed by Zeldovich due to the production of HCl being mainly through the reaction $H_2+Cl \rightarrow HCl+H$ and $Cl_2+H \rightarrow HCl+Cl$ and not via the dissociation of $Cl_2 \rightarrow Cl+Cl$ (which is pressure dependent) need to be confirmed by more precise measurements.

In this paper, the results of an experimental study of H_2-Cl_2 detonations are presented to verify the existence of pathological detonations in the H_2-Cl_2 system. Also, a more detailed kinetic study of the reaction mechanism in the ZND structure is made in an attempt to obtain a quantitative comparison between the experimental results and theoretical predictions of pathological detonations and hence confirm the kinetic mechanism as proposed by Zeldovich.

Experimental details

Accurate measurements of the detonation velocity were carried out in a 12.0m long cylindrical tube, with diameter 50.8mm. The length of the tube (200 diameters) is found to be sufficient to ensure that steady-state detonation can be achieved. Detonations were initiated via a high-energy electric spark from a 0.9µf-40 kV discharge. Four pressure transducers were used to measure the detonation pressure and the time of arrival of the detonation front in the final 8 meters of the tube to avoid the initial transient of the detonation after initiation. The detonation velocities were stable within 1% according to the x-t diagrams. The detonation pressure is a more accurate parameter to represent the detonation state since the detonation velocity is proportional to the square root of the Rayleigh line. Hence the detonation pressure was measured in the present study using PCB-113A24 and PCB-401A25 pressure transducers. The explosive mixtures of H_2-Cl_2 of the desired compositions are prepared by partial pressure and allowed to mix by diffusion for 3 days prior to using it. The accuracy in the mixture composition is less than 0.1% with the limitation due to the reading of the pressure gauges. The initial pressure of the mixtures studied varied from 3 kPa to 25 kPa.

Experimental results

Detonation velocities are first determined in the present tube in a mixture known to have an ideal behavior in accord with equilibrium CJ theory. Stochiometric C_2-H_2 mixtures at initial pressures ranging from 3 kPa to 25 kPa are used. We note that the experimental values are consistently slightly below the theoretical CJ predictions and this velocity deficit has been shown to be due to the boundary layer effect as predicted by the Fay-Dabora theory [5]. However, a much closer agreement is obtained between the measured and the CJ-predicted detonation pressure values.

Three compositions of H_2-Cl_2 with equivalence ratios of ϕ=0.666, ϕ=1.0 and ϕ=1.5, respectively lean, stochiometric and rich mixtures, are investigated. The experimental detonation velocities have been corrected for the boundary layer effects using the Fay-Dabora theory. According to these corrected results, we first note that for the three mixtures investigated, the detonation velocities are practically independent of the initial pressure in accord with the kinetic mechanism proposed by Zeldovich, i.e. HCl production independent of Cl_2 dissociation (Fig. 1).

As the predicted CJ detonation velocity values monotonically decrease with decreasing initial pressure, the largest pathological behaviors are observed at low initial pressures (Fig.2). Below initial pressures of 6 kPa, the experimental detonation velocities are at least 2% above the CJ predictions for all mixtures. This confirms that the role of Cl_2 dissociation is more dominant at low initial pressures.

The pathological effect is enhanced with an equivalence ratio below unity (excess Cl_2). For ϕ=0.666 and P_o=3.33 kPa, the experimental detonation velocity exceeds the CJ value by 7.9%. This is an additional indication of the important role of the Cl_2 dissociation, as the concentration of this molecule is larger for low equivalence ratios.

The detonation pressure is a more sensitive parameter than the detonation velocity. At high pressures (above 20 kPa), the experimental and CJ detonation pressure values are in very close agreement. However, as the initial pressure is lowered, the experimental detonation pressure ratio (P_{exp}/P_o) increases steadily, whereas the CJ detonation pressure ratio (P_{CJ}/P_o) remains nearly constant (small decrease). For the ϕ=0.666 mixture at P_o=5 kPa, an excess of almost 100% is obtained in detonation pressure as compared to the CJ predictions (Fig.3). This pressure excess is also a good indication of the pathological nature of the detonation.

The ZND structure

Unlike the equilibrium CJ states, pathological detonation states have to be determined by an analysis of the reaction zone structure. The eigenvalue detonation solution is found by satisfying the so-called “generalized CJ criterion” which requires the rate of heat release to vanish when sonic condition is reached. In normal detonations, the rate of heat release vanishes at the equilibrium CJ plane where sonic condition is reached. For the H_2-Cl_2 mixtures, the rate of heat release vanishes as the mixture undergoes a transition from exothermic to endothermic reactions. The remaining endothermic reactions of Cl_2 dissociation approach equilibrium beyond the sonic plane and thus does not affect the detonation velocity. This results in a higher than equilibrium pathological detonation velocity.

The theoretical values for the velocity and pressure for pathological detonations are computed from detailed kinetic consideration of the ZND structure using the “generalized CJ criterion” for non-equilibrium eigenvalue detonations [6]. This theoretical ZND calculation also confirms the existence of pathological detonations in the H_2-Cl_2 mixtures (Fig. 4). The predicted detonation velocities are found to be independent of the initial pressure for all 3 mixtures (Fig. 5), which is in agreement with both Zeldovich’s hypothesis and experimental results (Fig. 1). Zeldovich’s mechanism can be checked against the evolution of the chemical species within the reaction zone. A typical reaction profile in the reaction zone for H_2-Cl_2 detonation is shown in Fig. 6 where the product HCl approaches almost the equilibrium CJ value at the sonic plane, but the Cl_2 molecule and Cl radical at the sonic plane are not at the equilibrium values. Thus this delayed endothermic Cl_2 dissociation results in the pathological detonation observed in H_2-Cl_2.

The largest pathological behavior is observed at the lowest initial pressures, which is consistent with the experimental observations. The pathological effect is found to be largest with the ϕ=0.666 mixture, which is also in agreement with the experimental data. This again, is due to a higher concentration of Cl_2 molecules, whose slow dissociation is responsible for the delayed endothermic reaction phase.

The detonation pressures predicted by the ZND structure model are significantly above the CJ values (Fig.3). This was also the case for the experimental values. However, the ZND pressures are found to be nearly constant, whereas an important increase can be observed as the pressure is lowered in the experimental case.

The current chemical kinetics model thus succeeds in reproducing the qualitative detonation behavior of the H_2-Cl_2 mixture. However, the theoretical detonation velocity predictions are significantly above the experimental values and the ZND detonation pressures do not increase significantly for very low pressures like the experimental ones. For instance, the present model predicts an important pathological behavior even at 1 atmosphere for the stochiometric mixture (result also reported by Guénoche et al.[2]). Experimentally, no significant pathological behavior was observed for initial pressure above 20 kPa. These overestimations are most likely due to the weakness of the present chemical kinetics scheme. More recent data should be used.

Conclusion

The present study confirms the existence of pathological detonations in H_2-Cl_2 mixtures and that the effects are more pronounced at low initial pressures and low equivalence ratios where the dissociation of Cl_2 becomes important. The kinetic mechanism as proposed by Zeldovich responsible for pathological detonations is confirmed by the present experimental results and the kinetic analysis of the ZND reaction zone. The current kinetic scheme used in the ZND structure leads to predictions that are qualitatively in agreement with the experimental results. However, large quantitative discrepancies are observed. This is most likely due to the weakness of the chemical kinetic scheme.

Acknowledgements

This work is supported by the NSERC Grant #3347 and the authors acknowledge the contribution of Massimiliano Romano in the diagnostics.

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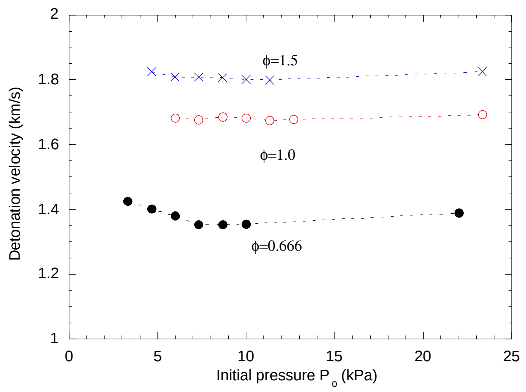

Figure 1: Experimental detonation velocities for the three H_2-Cl_2 mixtures.

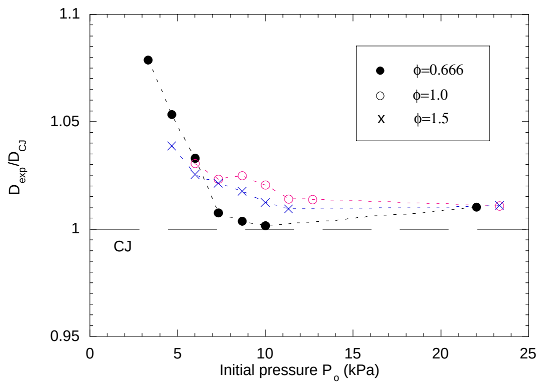

Figure 2: Normalized experimental detonation velocities for the three H_2-Cl_2 mixtures.

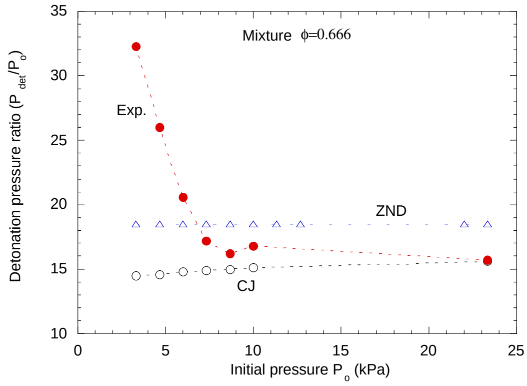

Figure 3: CJ, ZND and experimental detonation pressure ratios for the ϕ=0.666 H_2-Cl_2 mixture.

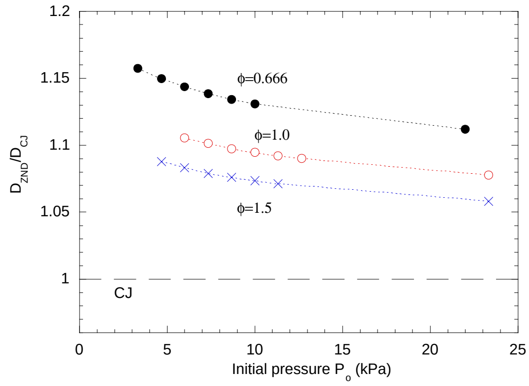

Figure 4: Normalized ZND detonation velocities for the three H_2-Cl_2 mixtures.

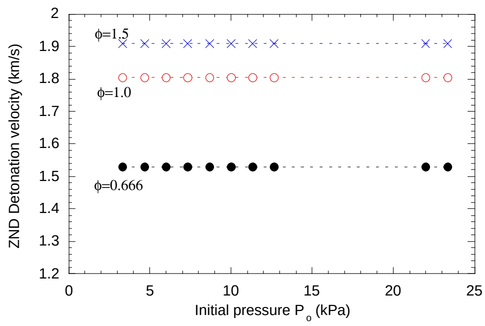

Figure 5: ZND Detonation velocities for the three H_2-Cl_2 mixtures.

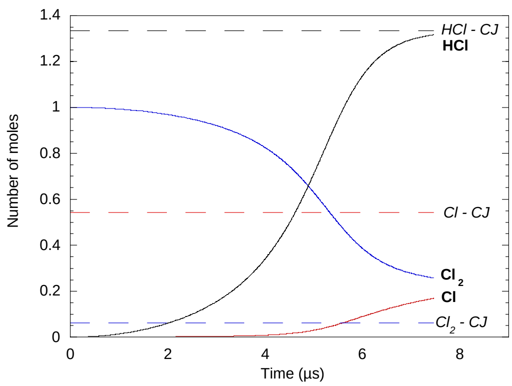

Figure 6: Concentration of HCl, Cl and Cl_2 within the reaction zone for the mixture H_2-Cl_2 ϕ=0.666, P_o=2 kPa. The dotted lines represent the equilibrium CJ predictions.