Effect of Free Radicals on the Transition from Deflagration to Detonation

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Introduction

It has been well established by the pioneering studies of Shchelkin [1] and Laffitte [2] that the run-up distance for transition from deflagration to detonation (DDT) can be drastically decreased by roughening the tube wall or by the insertion of obstacles (e.g., Shchelkin spiral) into the tube. Flame acceleration and DDT in obstacle-filled tubes have since then been investigated extensively from laboratory to large scale field tests of dimensions an order of magnitude larger [3].

The effect of chemical additives to promote (or retard) DDT has received relatively little attention to date. In the early study by Edgerton and Gates [4] a small amount of lead tetraethyl (TEL), an anti-knock agent, was added to a pentane-oxygen-nitrogen mixture to observe its influence on the pre-detonation distance. The results indicate that the effect of TEL is pressure dependent, and can either retard (increase in the pre-detonation period) or promote DDT. An interesting study was later carried by Shchelkin and Sokolik [5] on the effect of free radicals on DDT. They argued that the addition of free radicals should not influence the burning velocity or the thermodynamics of the mixture in the deflagration regime. In the detonation regime, however, where free radicals play an important role in the induction process, the addition of free radicals can promote the formation of detonation by a reduction in the induction time. Shchelkin and Sokolik carried out experiments in a mixture of pentane and oxygen in a heated tube. The mixture was rapidly introduced into the hot tube and was ignited immediately when cool flame oxidation of the mixture was detected. In their experiment, the free radicals are derived from the cool flame reactions. Shchelkin and Sokolik found that a sharp reduction in the pre-detonation distance is observed if ignition is effected immediately after the onset of cool flame oxidation. If ignition is delayed and the cool flame is allowed to proceed, however, the run-up distance is found to increase until the mixture failed to detonate at all for long delay times.

More recent studies of the role played by free radicals on the initiation of detonation were carried by Lee and coworkers. Both photo-chemical radical formation [6] and chemically generated radicals via the injection of a small amount of fluorine into a detonable gas [7], as well as rapid turbulent mixing of combustion products (which contain a fair amount of hot radicals) with a detonable gas [8] all led to the direct initiation of detonation. The important problem of the influence of free radicals on the run-up distance, as demonstrated by Shchelkin and Sokolik, has not been investigated since their pioneering efforts in 1937.

The present paper reports some recent results on the study of free radicals in the pre-detonation period. In the works of Shchelkin and Sokolik where cool flames or the mixing with combustion products to introduce free radicals to the detonable gas are employed, the initial condition prior to ignition could not be controlled due to the turbulent nature of the mixing process. Furthermore, there is also a temperature effect when cool flames (or the mixing with hot combustion products) are used to introduce free radicals. In the present study, photo-dissociation of Cl_2 is used to generate Cl in a H_2+Cl_2 mixture prior to ignition. The experimental scheme follows that for Patureau and Toong [9], who investigated the effect of non-equilibrium chemical reactions on the propagation of sound waves.

Experimental Details

The apparatus consists of a detonation tube 50 mm in diameter and 2.5 m long. Sufficient transmission of UV light at the wavelength corresponding to the peak absorption of Cl_2 (i.e., approximately 330 nm) through thin glass permits the use of a Pyrex tube rather than a quartz tube. The UV light is obtained from an F40BL ultraviolet fluorescent tube installed next to the detonation tube. The H_2+Cl_2 mixtures are prepared separately in a storage tank (based on the method of partial pressure to obtain the desired composition) and are allowed to mix by diffusion for at least 48 hours before use. The range of initial fill pressures used in the present study is 3-5 KPa. The choice for such low pressures is to retard the onset of detonation as much as possible within the confines of the apparatus, so that when free radicals are introduced via UV dissociation, any effect on the DDT process would be noticeable with current experimental resolution.

To obtain a reproducible pre-detonation period, a Shchelkin spiral (wire diameter 5 mm) of pitch approximately equal to one tube diameter is inserted into the detonation tube. Ignition is via a weak electric spark, and combustion front arrival times are deduced from the appearance of first light as monitored by PIN photodiodes spaced along the tube's length. Chlorine radical concentration is inferred from the transmitted UV light across the glass tube. The light is monitored via a Siemens SFH 530 UV selective sensor in series with a narrow optical bandpass filter centered at 334 nm (±12 nm at half amplitude). This provides a temporal history of the Cl_2 concentration during the pre-detonation period. A schematic of the apparatus is shown in Fig. 1.

Results

A series of control experiments were first carried out to observe the pre-detonation flame acceleration without free radical production from the UV photo-dissociation of Cl_2. A typical flame velocity evolution is shown in Fig. 2. In this figure, the velocity of the combustion front as measured by the photodiodes is shown as a function of distance for 8 separate trials with the same initial conditions. The typical value for the run-up distance in this case is about 560 mm (≈11 tube diameters), as deduced from the overdriven detonation velocities first observed at that location. After the onset of detonation, the steady velocity is 1600 m/sec as compared with the theoretical (Chapman-Jouget) value of 1756 m/sec. The deficit is due to the presence of obstacles in the tube. Without the Shchelkin spiral, large amplitude flame oscillations due to acoustic-flame interactions with the closed end tube are observed, and it becomes difficult to obtain reproducible run-up distances. With the spiral, the flame accelerates continuously to DDT and run-up distance is quite reproducible for given initial conditions.

Ignition and subsequent volumetric explosions by the UV light alone (without spark initiated DDT) was also investigated. An induction period is measured based on the time between UV light activation and that marked by a rapid rise in transmitted UV light, signaling auto-ignition. A typical transmitted UV light signal is shown in Fig. 3. The initial rise corresponds to the transient period associated with the activation of the fluorescent tube, and has a duration of 40-45 msec. The induction period is found to be dependent on the initial pressure, and in the pressure range studied it is found to vary roughly between 150 and 400 msec. Pre-detonation periods for DDT vary between 2 and 4 msec and are thus within the self-explosion delay time of the mixture due to UV radiation alone. From the signal observed, it is found that the Cl radical concentration remains fairly constant during the induction period, but drops rapidly during auto-ignition as indicated by the rapid rise in transmitted UV light after 300 msec.

Finally, the influence of free radicals on the pre-detonation regime of the flame propagation is shown for 7 separate trials with the same initial conditions in Fig. 4. The UV light was first activated, and after a delay corresponding roughly to the induction period of the mixture for thermal explosion alone (≈200 msec), spark ignition was effected. With photo-dissociation, and the consequent presence of free radicals during the DDT process, the run-up distance is reduced to about 460 mm (≈9 tube diameters). The steady detonation velocity obtained after onset is approximately 1600 m/sec. Thus, other than an increase in velocity fluctuations after DDT, it is found that the presence of free radicals has no influence on the detonation velocity.

Conclusion

Although the present experimental results do suggest a reduction in the DDT run-up distance when free radicals are present, the decrease is only on the order of 20%. This indicates that free radicals do not have any influence on flame propagation (as pointed out by Shchelkin and Sokolik [5]), and can only affect the regime immediately before the onset of detonation when auto-ignition is imminent. Since the run-up distance is predominantly due to flame propagation, its reduction in the presence of free radicals is not significant.

Acknowledgements

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References

1. Shchelkin K.I. (1946) "Effect of Roughness of the Surface in a Tube on Origination and Propagation of Detonation in Gases," *Journal of Experimental and Theoretical Physics* **10**.
2. Laffitte P. (1923) "Sur la formation de l'onde explosive," *Comp. Rend. 176*, Académie des sciences, p. 1392-1395.
3. Lee J.H.S. and Moen I. (1980) "The Mechanism of Transition from Deflagration to Detonation in Vapor Cloud Explosion," *Prog. Energy Combust. Sci.* **6**, pp. 359-389.
4. Edgerton A. and Gates S. (1927) "On Detonation of Gaseous Mixtures of Acetylene and of Pentane," *Proc. Roy. Soc.* **A114**, pp. 137-152.
5. Shchelkin K.I. and Sokolik A.S. (1937) *ZhFKh* **10**, pp. 479-484.

6. Lee J.H., Knystautas R. and Yoshikawa N. (1978) "Photochemical Initiation of Gaseous Detonations," *Acta Astronautica* **5**, pp. 971-982.
7. Murray, S.B., Moen, I.O., Thibault, P.A., Knystautas, R., Lee, J.H.S. and Sulmistras, A. (1991) "Initiation of Hydrogen-Air Detonations by Turbulent Fluorine-Air Jets," *Prog. Astro. Aero.* **133**, pp. 91-117.
8. Knystautas, R., Lee, J.H. and Moen, I. (1978) "Direct Initiation of Spherical Detonation by a Hot Turbulent Gas Jet," *17th Symp. Int. Combust. Proc.*, pp. 1235-1245.
9. Patureau J.-P., Toong T.-Y. and Garris C.A. (1976) "Experimental Investigation of Acoustic-Kinetic Interactions in Non-Equilibrium H_2-Cl_2 Reactions," *16th Symp. Int. Combust. Proc.*, pp. 929-938.

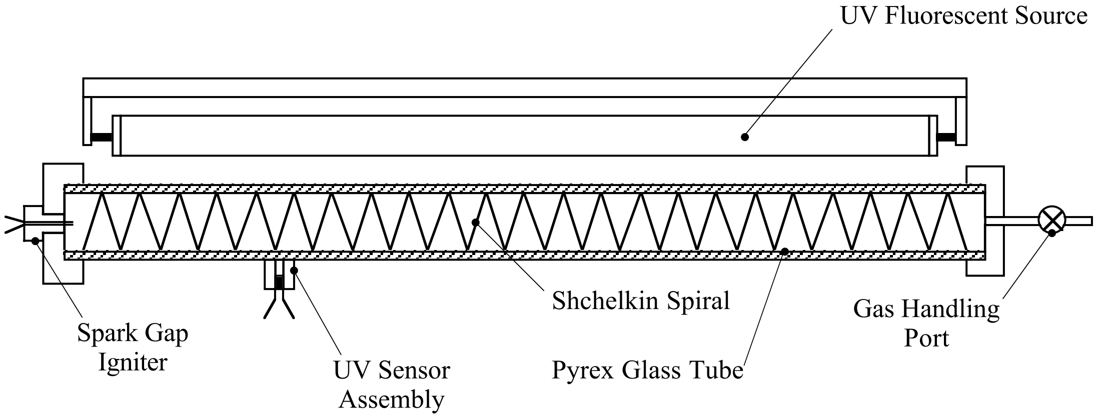

Fig. 1. Schematic of apparatus.

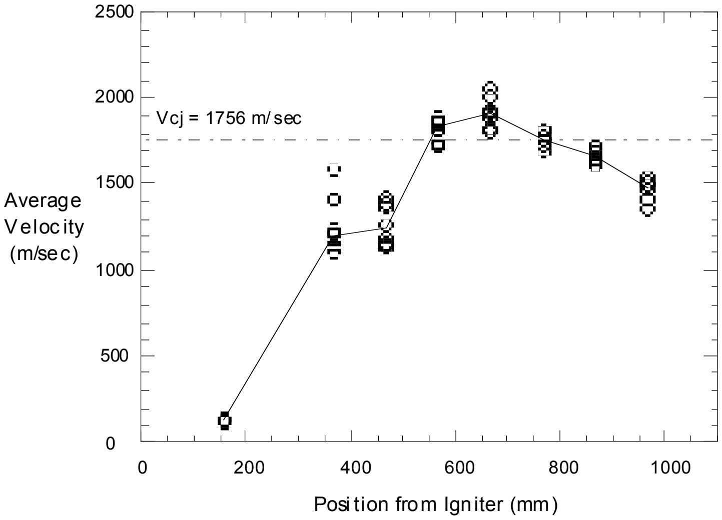

Fig. 2. *V-x* plot of DDT in H_2-Cl_2 with initial conditions $\phi = 1.5$, $P_i = 4.8$ Kpa and $T_i = 298$ K

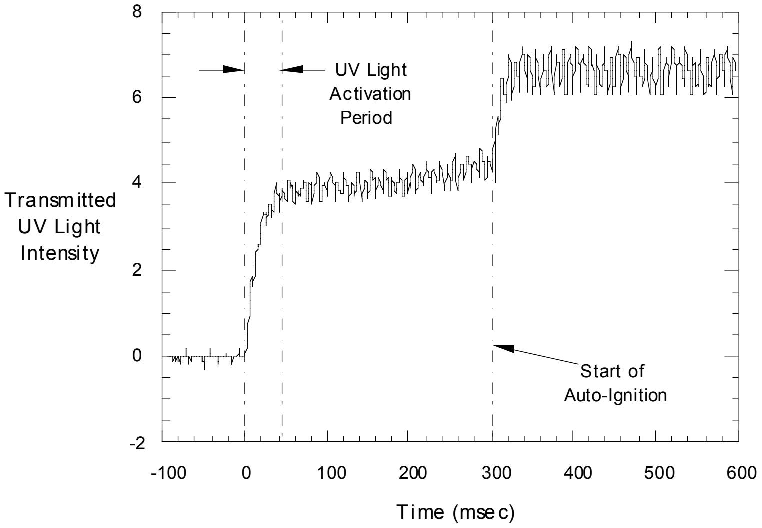

Fig. 3. Transmitted UV light in photochemically initiated volumetric explosion of H_2-Cl_2 with initial conditions $\phi = 1.5$, $P_i = 4.8$ Kpa and $T_i = 298$ K (without spark ignition)

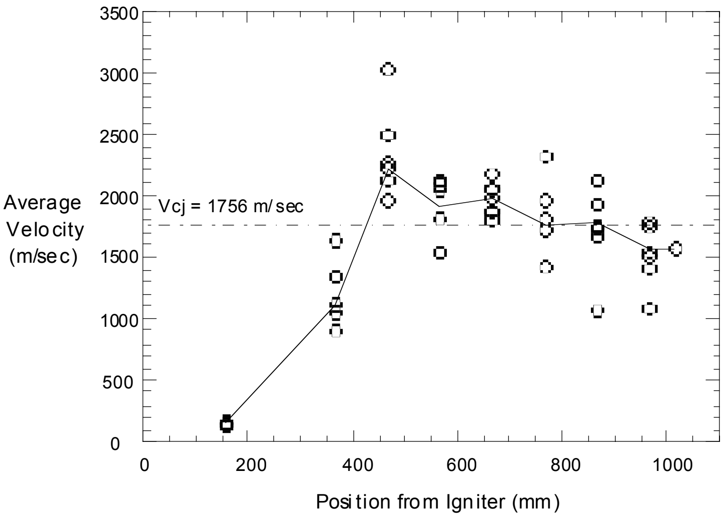

Fig. 4. V-x plot of DDT in H_2-Cl_2 under UV irradiation with initial conditions $\phi = 1.5$, $P_i = 4.8$ Kpa and $T_i = 298$ K