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# The effect of free radicals on the transition from deflagration to detonation

by

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A thesis submitted to the Faculty of Graduate Studies and Research In partial fulfilment of the requirements for the degree of Master's in Engineering

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## Abstract

The effect of free radical pre-sensitization on the transition from deflagration to detonation (DDT) in a combustible gas has been studied experimentally. Sensitization was achieved before spark ignition and DDT by illuminating a quiescent mixture of hydrogen and chlorine with a weak ultraviolet source. The arrival time of the reaction front was monitored by means of discretely located optical sensors along the length of the detonation tube.

While no observable changes are produced during the early stages of the flame acceleration process, it is found that radical seeding promotes the onset of detonation through a reduction in run-up length and time. This is in accord with the generally accepted view that flame acceleration is mostly governed by molecular and turbulent transport. The photochemical initiation of chain reactions ahead of the flame accelerates the induction kinetics of the mixture. Shock induced auto-ignition is therefore facilitated, thereby promoting DDT during the period of onset.

## Résumé

L'effet de la pré-sensibilisation par radicaux libres sur la transition déflagrationdétonation dans un mélange combustible gazeux fit l'objet d'une étude expérimentale. Un mélange hydrogène-chlore fut sensibilisé à l'aide d'une faible source de rayons ultraviolets avant que ne surviennent l'allumage et l'éventuelle transition flammedétonation. Le temps d'arrivée du front de réaction fut mesuré à partir de sondes optiques disposées sur la longueur du tube de détonation.

Aucun effet sur l'accélération de la flamme, initiallement lente, ne fut observé. Néanmoins, la sensibilisation par radicaux libres accélère le procédé d'amorçage en réduisant la distance et le temps de transition. Cette observation soutient l'idée généralement acceptée, selon laquelle l'accélération d'une flamme initiallement lente est gouvernée par les mécanismes de la turbulence et de la diffusion moléculaire. L'initiation photochimique de réactions en chaîne devant la flamme accélère la cinétique chimique inductive du mélange. Ceci facilite l'amorçage par onde de choc et, par conséquent, une onde de détonation peut se former plus rapidement durant la période finale de transition.

iii

## Acknowledgements

First and foremost, I would like to express deep gratitude to my supervisor, Prof. John Lee, who supported this project and inspired me throughout the course of my studies. Many thanks to my colleague and friend Prof. Andrew Higgins who, through his world class expertise in the field, guided me throughout the entire course of this research effort. This entire project would have been an impossibility without the electronic "wizardry", unwavering patience and genuine devotion of my good friend Massimiliano Romano. The technical advice, as well as the numerous stimulating discussions entertained with my colleague Dr. Samuel Goroshin, was also greatly appreciated.

The photographic advice provided by Dr. Harald Kleine and Keith Edwards are gratefully acknowledged. The technical support provided by the crew of the Machine Tool Lab (Tony, Louis, Dan and Roy) as well as the Undergraduate Lab (Gary, John and Ray) was invaluable. Special thanks to Gary Savard who taught me the "tricks of the trade", and who was extremely understanding in my frequent requests for machining parts. I want to thank Della Maharajh for providing the essential logistics support and for her patience in handling the "Suwupugs".

Last but certainly not least, I would like to thank all the members of the Shock Wave Physics Group (SWPG) who, through their enthusiasm and support, made the time spent at McGill very enjoyable.

## Table of Contents

Abstract	ii
Résumé	iii
Acknowledgements	iv
Table of Contents	v
List of Figures	vii
Chapter 1 Introduction	1
Chapter 2 Experimental Details and Procedure	10
2.1 Experiment overview	10
2.2 Mixture selection and preparation	11
2.3 UV radiation source	13
2.4 Diagnostics	14
2.4.1 Optic probes for time of arrival (TOA) measurements	15
2.4.2 UV sensor for transmitted UV light measurements	15
2.4.3 Cl <sub>2</sub> concentration estimates from UV light measurements	15
2.5 Pre-sensitization/ignition circuitry	18
Chapter 3 Results and Discussion	27
3.1 DDT without UV pre-sensitization	27
3.2 Photochemical reaction without spark ignition	28
3.3 The effect of free radicals on DDT	31
3.4 Lee criterion for self-initiation	34
Chapter 4 Conclusions	56

References	58
Appendix A Modification of ballast circuitry	62
A.1 Working principle of fluorescent tube	62
A.2 Working principle of ballast	63
A.3 Ballast circuitry and modification	63
Appendix B Optical probe response	67
B.1 Phototransistor response	67
B.2 Relative probe response	67
Appendix C Data reduction	71
C.1 Time-of-arrival (TOA)	71
C.2 Average reaction front velocity (Vaverage)	72
C.3 Characteristic run-up length ( $x^*$ and $x^*_{UV}$ )	73
C.4 Characteristic run-up time (t* and t $*_{UV}$ )	74
C.5 Photochemical explosion time (tinduction)	75

## List of figures

- Fig. 1.1 Experimental scheme of the investigation by Shchelkin and Sokolik [14]
- Fig. 1.2 Typical result by Shchelkin and Sokolik [14] in a mixture of pentane and oxygen with a coefficient of excess air of  $\alpha = 0.9$  and a pressure and temperature of 320 torrs and 335° C respectively
- Fig. 1.3 Experimental scheme of the current investigation
- Fig. 2.1 Schematic of detonation tube
- Fig. 2.2 Schematic of time-of-arrival (TOA) probes mounted on detonation tube
- Fig. 2.3 Enlarged view of optic probe assembly
- Fig. 2.4 Overall UV sensing setup
- Fig. 2.5 Enlarged view of UV sensor assembly
- Fig. 2.6 Cl<sub>2</sub> absorption coefficient as a function of wavelength at room temperature
- Fig. 2.7 Transmitted UV light as a function of Cl<sub>2</sub> concentration at 22°C (UV sensor calibration data)
- Fig. 2.8 Schematic of ignition timing components
- Fig. 3.1 Detonation velocity data in  $1.5 H_2 + Cl_2$  mixtures at 295 K initial temperature
- Fig. 3.2 x-t diagrams of DDT in  $1.5 H_2 + Cl_2$  mixtures at 4 kPa and 295 K initial conditions
- Fig. 3.3 x-t diagrams of DDT in  $1.5 H_2 + Cl_2$  mixtures at 4.8 kPa and 295 K initial conditions
- Fig. 3.4 *V-x* diagrams of DDT in  $1.5 H_2 + Cl_2$  mixtures at 4 kPa and 295 K initial conditions

- Fig. 3.5 *V-x* diagrams of DDT in 1.5 H<sub>2</sub> + Cl<sub>2</sub> mixtures at 4.8 kPa and 295 K initial conditions
- Fig. 3.6 Typical transmitted UV light data for  $1.5 H_2 + Cl_2$  mixtures at 4.8 kPa and 295 K initial conditions
- Fig. 3.7 Typical Cl<sub>2</sub> concentration data for 1.5 H<sub>2</sub> + Cl<sub>2</sub> mixtures at 4.8 kPa and 295 K initial conditions
- Fig. 3.8 Photochemical induction time data for  $1.5 H_2 + Cl_2$  mixtures at 4.8 kPa and 295 K initial conditions
- Fig. 3.9 x-t diagrams of DDT in  $1.5 H_2 + Cl_2$  mixtures at 4 kPa and 295 K initial conditions with UV pre-sensitization
- Fig. 3.10 x-t diagrams of DDT in  $1.5 H_2 + Cl_2$  mixtures at 4.8 kPa and 295 K initial conditions with UV pre-sensitization
- Fig. 3.11 *V-x* diagrams of DDT in  $1.5 H_2 + Cl_2$  mixtures at 4 kPa and 295 K initial conditions with UV pre-sensitization
- Fig. 3.12 *V-x* diagrams of DDT in 1.5 H<sub>2</sub> + Cl<sub>2</sub> mixtures at 4.8 kPa and 295 K initial conditions with UV pre-sensitization
- Fig. 3.13 Comparative V-x diagrams demonstrating the effect of UV pre-sensitization for 1.5  $H_2 + Cl_2$  mixtures at 4.8 kPa and 295 K initial conditions
- Fig. A.1 Electric circuitry of fluorescent tube ballast
- Fig. A.2 Schematic of ballast modification
- Fig. B.1 Typical OP505 phototransistor signal monitoring detonation in a mixture of  $1.5 H_2 + Cl_2$  at 4.8 kPa and 295 K initial conditions

- Fig. B.2 Comparative traces showing signal start-of-rise of both phototransistor and PIN photodiode located at the same distance from the igniter (both probes are monitoring detonation in a mixture of  $1.5 H_2 + Cl_2$  at 4.8 kPa and 295 K initial conditions)
- Fig. C.1 Typical PIN photodiode traces showing DDT in a mixture of  $1.5 H_2 + Cl_2$  at 4.8 kPa and 295 K initial conditions
- Fig. C.2 Optic probe view angle schematic
- Fig. C.3 Effect of scattered light on optic probe view angle
- Fig. C.4 Features of the x-t diagram
- Fig. C.5 Schematic of possible DDT scenarios
- Fig. C.6 Scenarios involving same run-up time but different run-up lengths
- Fig. C.7 Typical transmitted UV light signal to get photochemical induction time  $(t_{induction})$  before auto-ignition and thermal explosion in a mixture of  $1.5 H_2 + Cl_2$  at 4.8 kPa and 295 K initial conditions

## Chapter 1: Introduction

In a large number gaseous fuel/oxidizer mixtures, a flame will accelerate and eventually transit to detonation. Although there is no quantitative theory to predict the exact transition length, current knowledge permits a qualitative picture of the deflagration to detonation transition (DDT) process. While an initially laminar flame propagates only at speeds typically less than 10 m/sec, the burning rate can be drastically increased if the flame is made turbulent. The onset of turbulence in the flame front stems from two mechanisms (Lee [1]). One is due to the onset of turbulence in the flow of unburned gases ahead of the flame when the Reynolds number becomes sufficiently high, and the other is due to the interaction of pressure/shock waves with the flame. Both mechanisms lead to the distortion of the flame into a highly wrinkled structure. This increase in flame area is accompanied by an increase in the heat release rate, which gives rise to a higher displacement rate of unburned gases ahead of the flame and generates stronger pressure waves. The final process of the onset of detonation is one of a highly turbulent flame brush propagating behind a series of shock waves. The termination of the deflagration regime is marked by the sudden appearance of the detonation, in some localized region within the turbulent flame zone. Typical photographic records of flame acceleration and DDT can be found in the works of Urtiew and Oppenheim [2].

The effect of tube roughness on the transition length has been studied in the pioneering work of Laffitte [3], who found that detonation onset occurs much earlier

when a trail of sand is laid along the length of the wall of a flame tube. A more extensive study of the effect of wall roughness on DDT and detonation propagation was later performed by Shchelkin [4], who inserted wire spirals into glass explosion tubes and, as a result, observed a systematic decrease in the DDT length. It appears that the large scale turbulence generated by the obstacles is broken down to finer scale upon interacting with the shock waves that reflected off these obstacles. The resulting effect is a mechanism of "shock induced enhanced mixing" which promotes turbulent burning rate and, consequently, shortens the run-up length.

While the transition from deflagration to detonation has been studied extensively over the years, the effect of chemical additives on the transition process has received relatively little attention to date. Previous investigations involved the use of chemical inhibitors in combustible mixtures to study their effect on the propagation of flames and detonation waves. These inhibitors consisted of flame suppressants and retardants such as  $CF_3Br$ ,  $C_2F_4Br_2$ , etc., and also antiknock agents like lead tetraethyl, diethyl selenide, etc. that reduce the concentration of free radicals and, as a result, slow down reaction rates. Their effect on flames, however, differs from their effect on detonations.

The influence of halogenated compounds on the propagation of fast turbulent flames and quasi-detonations was studied by Johnston et al. [5] and Gmurczyk and Grosshandler [6]. Johnston found that the effect is a systematic decrease in the velocity as well as a narrowing of the propagation limits. Gmurczyk found that the effect is dependent upon the type and concentration of inhibitor used, as well as the mixture composition, and can either retard or promote the propagation of fast flames and quasidetonation. The effect of inhibiting compounds on established detonations was also investigated. Moen et al. [7] found that the addition of small amounts of CF<sub>3</sub>Br has a slight sensitizing effect on the critical tube diameter problem, namely, he observed a decrease in the critical tube diameter. Similarly, Vandermeiren and Van Tiggelen [8] also observed CF<sub>3</sub>Br to have a sensitizing effect on self-sustained detonation through a slight decrease in the cell size and a slight increase in the detonation velocity. Borisov et al. [9] found that the addition of  $C_2F_4Br_2$  to hydrocarbon/air mixtures causes the flammability limits to narrow differently from detonability limits. He explains that although brominated compounds are effective suppressors of atomic hydrogen radicals (H) within the low temperature pre-heat zone of flames, high temperature shock heating leads to the decomposition of the inhibitor into chain carrying free radicals. Since decomposition rates of halogenated inhibitors are usually higher than that of hydrocarbon fuels, chain initiation is promoted.

As for the effect of additives on DDT, Egerton and Gates [10,11], Shchelkin and Sokolik [12] and Nzeyimana, Vandermeiren and Van Tiggelen [13] have studied their influence on the run-up length (i.e., the transition distance). The experiment of Egerton and Gates involved the addition of small amounts of TEL (i.e., lead tetraethyl or Pb(Et)<sub>4</sub>), an antiknock agent, to a mixture of pentane and oxygen diluted with nitrogen (i.e.,  $C_5H_{10} + 8O_2 + 2N_2 + 0.13\%$ TEL) with an initial pressure of 1 atm. The results show a reduction in run-up length instead of an increase as expected from the antiknock properties of TEL. On the other hand Shchelkin and Sokolik, who used the same mixture with the same antiknock agent (though they used a higher TEL content, namely, 1.2%), did their experiments at lower initial pressures (i.e., 0.65-0.276 atm.) in a larger sized tube. In this case, the results showed an increase in the run-up length. Later in the investigation of Nzeyimana, Vandermeiren and Van Tiggelen, addition of a small amount of CF<sub>3</sub>Br inhibitor to a stoichiometric mixture of CO/H<sub>2</sub>/O<sub>2</sub>/Ar produced no observable change on the DDT length.

While the goal of all the above experiments was the suppression of free radicals via additives, one can also look at the effect of seeding a mixture with free radicals on DDT. The only experiment to date which involved the direct production of free radicals within the mixture before ignition and DDT, was that of Shchelkin and Sokolik [14]. In studying the effect of TEL on the deflagration to detonation transition in pentane/air mixtures, Shchelkin and Sokolik [12] concluded that DDT is governed by a process of "…primary oxidation taking place ahead of the flame front…". In order to find out what stage of this oxidation process is mostly responsible for the formation of a detonation, they proceeded with another experiment where the focus was on the so-called chemical pre-sensitization stage which, from chemical kinetics, would correspond to chain-initiating elementary reactions, where free radicals are first formed.

Fig. 1.1 is a schematic of their experimental procedure. A mixture of pentane and oxygen was injected into a heated tube (1). Heat transfer from the hot walls results in cool flame oxidation of the mixture (2), thereby producing radicals (3). After a

prescribed amount of time, spark ignition was effected and the flame trajectory (4) as well as the eventual onset of detonation (5) were monitored via streak photography.

Fig. 1.2 shows the results of a typical test series. It is a plot of detonation run-up length S (in cm) as a function of spark ignition time (in sec) after mixture insertion in the heated tube. The cool flame induction period was found to fluctuate within about 0.2 sec and is thus represented by a shaded region. Initial conditions of pressure and temperature inside the tube were varied between 250-370 torrs and 325-400° C respectively. By igniting the mixture at various stages of the cool flame process, the run-up length was found to change. The authors mention that during the onset of cool flame oxidation, the concentration of peroxide radicals reaches a maximum while during the later stages of the process, concentrations of aldehydes and carbon monoxide increase at the expense of peroxides. They attribute the sudden reduction in run-up length when ignition is effected immediately after onset of cool flame to the peak concentration of peroxides. On the other hand, increase in run-up distance or failure to detonate at all when ignition is effected a long time after the appearance of cool flame, is associated with a reduction of peroxide concentration, as well as with a dilution of the mixture with cool flame products. The latter results in dissipation of part of the chemical heat release associated with the initial hydrocarbon. They conclude by stating that cool flame oxidation gives rise to a change in the kinetic properties of the original mixture, thereby leading to a change in detonation run-up distance.

While the results due to Shchelkin and Sokolik are intriguing, they could not control the production nor the distribution of free radicals along their tube (i.e., due to non-uniform heating of the mixture as it is being injected). Consequently, the concentration of free radicals along the tube may not have been uniform.

In order to further investigate the effect of free radical seeding on the DDT process, experiments were carried out on mixtures of gaseous hydrogen and chlorine. As shown in Fig. 1.3, the choice for this system permits the use of a UV source to photochemically dissociate molecular chlorine into atomic chlorine radicals (1). It also allows, in principle, uniform pre-sensitization of an initially quiescent mixture, as opposed to the investigation of Shchelkin and Sokolik which involved both injecting and pre-sensitizing the mixture at the same time, thereby resulting in a less controllable experiment. Once the system has been irradiated and radicals produced (2), a flame is lit (3) and the DDT process monitored (4). The research reported in this thesis is an experimental investigation of the effect of photochemically produced free radicals on detonation run-up in a combustible mixture.



Fig. 1.1 Experimental scheme of the investigation by Shchelkin and Sokolik [14]



Fig. 1.2 Typical results by Shchelkin and Sokolik [14] in a mixture of pentane and oxygen with a coefficient of excess air of  $\alpha = 0.9$  and a pressure and temperature of 320 torrs and 335° C respectively



Fig. 1.3 Experimental scheme of the current investigation

## **Chapter 2: Experimental Details and Procedure**

In the current study, photo-dissociation was used as a means to pre-sensitize a  $H_2$ -Cl<sub>2</sub> mixture whose chemical kinetics is fairly well understood (Rollefson and Burton [15], Kondrat'ev [16], Calvert and Pitts [17], Noyes and Leighton [18], Ellis and Wells [19]).

#### 2.1 Experiment overview

A schematic of the apparatus used in this study is illustrated in Fig. 2.1. The H<sub>2</sub>-Cl<sub>2</sub> mixture was introduced into an evacuated Pyrex glass tube of dimensions 2.45 m in length by 51 mm inner diameter. A fluorescent "UV Black Light" was used to irradiate and pre-sensitize this mixture. After a preset UV irradiation time, ignition was achieved via an electrical spark at one end of the Pyrex tube. The flame front time-trajectory was monitored via luminosity probes spaced along that tube. Since the run-up length in smooth tubes is very irreproducible, it was found that increasing wall roughness in the form of periodically spaced obstacles in the tube could yield reproducible and much reduced run-up lengths. For the obstacles, a hand made aluminum Shchelkin spiral with pitch  $\approx$  1 tube diameter and wire cross section diameter = 4.25 mm was used. This corresponds to a blockage ratio of about 0.31. Note that in order to prevent the mixture from reacting prematurely, the apparatus as shown in Fig. 2.1 along with the diagnostics were shielded from exterior light by placing them in a flat black wooden enclosure. In addition, all lights in the laboratory were turned off before each trial.

## 2.2 Mixture selection and preparation

The mixture used throughout the present investigation was  $1.5H_2 + Cl_2$  with an initial temperature of  $T_i = 295$  K, and at two initial pressures, namely,  $P_i = 4$  and 4.8 kPa. Detonation under these initial conditions produces cell sizes ranging between about 9 and 15 mm (Knystautas and Lee [20], Kaneshige and Shepherd [21]) which is below the inner diameter of the tube with the obstacles (i.e.,  $ID \approx 51$  mm and  $ID_{with obstacles} \approx 42$  mm). A UV source was used to photochemically dissociate molecular chlorine into atomic chlorine radicals. In order to increase luminosity from the flame front, a number of trials involved seeding the mixture with a small amount of  $C_2H_2$ . All gases used were of the Matheson High Purity grade (i.e., 99.5% pure). The initial pressures of the mixture in the experiment were monitored via a mercury U-tube manometer with an accuracy of  $\pm \frac{1}{2}$  torr. It was necessary to use a small 3 cm column of Edwards High Vacuum pump oil as a buffer to prevent  $Cl_2$  from reacting with the mercury. To compensate for the increased hydrostatic pressure generated by this addition, an equal height of oil was also inserted on the opposite arm of the U-tube manometer.

The mixtures were prepared in separate mixing tanks by the method of partial pressure, and allowed to mix by diffusion for 48 hours. An Omega PX-302-15AV pressure transducer (with an accuracy of  $\pm 6.5$  torrs) was used to monitor the tank pressure during filling. Turbulent vortices associated with the jetting of one component into the other, as well as natural convection currents setup by the largely different masses of both gases will give rise to some initial mixing. Yet, it is still possible to obtain a

rough upper limit estimate of the time necessary for both components to mix solely via diffusion by invoking the following approximation

$$\tau_{mixing} = \frac{L^2}{D}$$
 Eq. 2.1

where,

L = Total diffusion length (vessel cross section)

D = Mass diffusion coefficient

Eq. 2.1 is derived from a dimensional analysis of the 1-D differential form of the mass conservation equation. Holman [22] and Gilliland [23] provide a semi-empirical relation for the diffusion coefficient, namely,

$$D = 435.7 \frac{T^{3/2}}{p(V_{H_2}^{1/3} + V_{Cl_2}^{1/3})^2} \sqrt{\frac{1}{M_{H_2}} + \frac{1}{M_{Cl_2}}} \quad \text{Eq. 2.2}$$

where,

 $M_{H_2} = 2.01588$  g/mol (molar mass of H<sub>2</sub>)

 $M_{Cl_2} = 70.9054$  g/mol (molar mass of Cl<sub>2</sub>)

 $V_{H_2} = 14.3$  (atomic volume of H<sub>2</sub>)

 $V_{Cl_2} = 21.6$  (atomic volume of Cl<sub>2</sub>)

T = 295 K (initial mixing tank temperature)

P = 300000 Pa (initial mixing tank pressure)

With these values in mind, Eq. 2.2 gives  $D = 0.193 \text{ cm}^2/\text{sec.}$  When laying on its side, the mixing tank had a cross diameter of about 20 cm. Using this as the characteristic length for Eq. 2.1, the mixing time is on the order of  $\tau_{mixing} = 35$  minutes. Since the actual mixing period was 48 hours, it can be safely assumed that both components were sufficiently mixed.

### 2.3 UV radiation source

In the previous investigation of Lee, Knystautas and Yoshikawa [24], xenon flash lamps were used to photo-ignite a  $H_2/Cl_2$  mixture. In the present experiments, however, photo-dissociation is used as a means to achieve pre-sensitization. Hence, only a small amount of photo-dissociated  $Cl_2$  molecules is needed. The technique used was similar to that of Patureau, Toong and Garris [25], who studied the effect of chemical kinetics on the propagation of sound waves. The source consisted of a General Electric fluorescent F40BL UV "Black Light" tube. Powered by the ballast (i.e., transformer for fluorescent tubes) of a standard fluorescent fixture (120VAC, 40Watts) the F40BL can generate incident energy intensities ranging from 1 to 4 milliwatts/cm<sup>2</sup> when located within 6 inches of the target. One of the inherent drawbacks of using this kind of UV source is the long time required to reach steady light emission; typically on the order of a few seconds for a "cold start". A modification was therefore required to shorten this "start up" transient. It basically consisted of the following: the cathode voltage was first applied in order to warm up the electrodes without turning on the lamp, while the larger arc voltage across the tube was then turned on a few seconds later. This modification was found to reduce the overall start-up time from a few seconds down to about 45 msec.

A detailed explanation of this alteration is covered in appendix A. Note that only the first half of the detonation tube (i.e., the test section) was exposed to UV, since this is where DDT was expected to occur.

### 2.4 Diagnostics

Streak photography cannot be used for the  $H_2/Cl_2$  system because of the low intensity light emission by the flame. An attempt to increase the luminosity by seeding this mixture with a hydrocarbon was tried. An addition of 1% (molar basis) of  $C_2H_2$  was found to produce insufficient light for streak photography. Also, since the  $H_2/Cl_2/C_2H_2$ mixture slowly decomposes within the mixing tank, no further experiments were conducted with this composition.

Another much simpler method to detect onset of detonation, is the soot coated foil technique. This idea uses soot coated surfaces (e.g., mylar or aluminum sheets) upon which the detonation, once formed, leaves a record of its passage in the form of a cellular or "fish scale" pattern. It is generally recognized that this "writing" process is due the rearrangement of the soot by the shock triple points within the detonation. This technique, though simple and very reliable, is intrusive and thus was not used in the foregoing experiments. Luminosity probes spaced along the detonation tube for discrete time of arrival (TOA) measurements were therefore used exclusively for the entire course of this study. These, as well as the UV sensor assembly, will be discussed in the following sections. Note that care was taken to locate all probes out of the line of sight of the Shchelkin spiral.

14

#### 2.4.1 Optic probes for time of arrival (TOA) measurements

The two sensors that were found to be adequate for the H<sub>2</sub>/Cl<sub>2</sub> system are the Motorola OP505 phototransistor and the EG&G silicon N-type PIN C30831E photodiode. The way in which these probes were mounted on the tube is illustrated in Figs. 2.2 and 2.3. OP505 sensors were fixed to hollowed out black Delrin dowels and "looked" directly at the glass tube. PIN photodiodes, on the other hand, monitored the events in the glass tube through fiber optic cables connected to the black Delrin cylinders. An aluminum bar comprising a long array of holes spaced at 25 mm (1/2 tube diameter) permitted interchangeable probe positions along the tube. A more detailed discussion regarding the response of these probes is covered in appendix B.

#### 2.4.2 UV sensor for transmitted UV light measurements

During an experiment, the mixture was irradiated with UV and the transmitted UV light monitored via a Siemens SFH530 UV sensor located on the opposite side of the tube. A Corion P10-334-A UV bandpass filter (transmits radiation at  $334\pm10$  nm) was used in front of the UV sensor in order to monitor the radiation corresponding to the peak absorption of Cl<sub>2</sub>. Such an assembly is shown in Figs. 2.4 and 2.5.

#### 2.4.3 Cl<sub>2</sub> concentration estimates from UV light measurements

The  $Cl_2$  consumption rate can be deduced from transmitted UV light measurements by means of the Beer-Lambert absorption law, which states,

$$\frac{I}{I_o} = e^{-\alpha cd}$$

where,

*I* = transmitted light intensity

 $I_o$  = incident light intensity

 $\varepsilon$  = absorption coefficient

c = concentration in moles per unit volume

d = thickness of absorbing layer

The absorption coefficient  $\alpha$  is determined by the nature of the absorbing substance and the wave length of the light under consideration, and must be constant for the above law to hold true. This law, therefore, is theoretically exact only for a single frequency and a single molecular species. The absorption of hydrogen chloride (HCl) lies below 215 nm (Ellis and Wells [19]) and molecular hydrogen (H<sub>2</sub>) is found to be completely transparent down to about 112 nm (Noyes and Leighton [18], Ellis and Wells [19]). With these values in mind, H<sub>2</sub> and HCl will be transparent to the UV light employed which emits above 300 nm and, as a result, will not interfere with the Cl<sub>2</sub> concentration measurements. The UV source utilized was not monochromatic and therefore, use of the Beer-Lambert law will constitute only a rough approximation of the Cl<sub>2</sub> concentration count. Fig. 2.6 shows both the absorption spectra of Cl<sub>2</sub> and the emission spectral range of the UV light. Note that in order to match the units used in the current investigation, the scale of the absorption coefficient has been converted from its original sources (von Halban and Siedentopf [26], Gibson and Bayliss [27]). With the use of a bandpass filter, the UV sensor only "sees" radiation with a wavelength of 334 nm. From Fig. 2.6, this corresponds to an absorption coefficient of about 14.94 m<sup>3</sup>/<sub>mol m</sub>.

Calibration of the UV sensor was achieved by introducing a known quantity of  $Cl_2$  into the Pyrex detonation chamber. The UV lamp was then turned on and the transmitted light signal measured. Following the evacuation of the glass chamber, the maximum transmittable UV light was finally measured. This was done for a number of  $Cl_2$  concentrations so that a plot of the ratio of transmitted light to maximum transmittable light was obtained as a function of  $Cl_2$  concentration. Fig. 2.7 shows such a calibration curve. Also demonstrated in this figure is a curve fit of the datapoints, which is exponential as with the form of the Beer-Lambert absorption law. It is given by,

$$\frac{I}{I_o} = e^{-\alpha cd} = e^{-0.66c}$$

For an absorbing layer equal to the tube cross section (i.e., d = 50.7 mm), the above equation yields an absorption coefficient of about 13.0 m<sup>3</sup>/<sub>mol m</sub>, which is about 13% less than the value of 14.94 m<sup>3</sup>/<sub>mol m</sub> obtained from Fig. 2.6. This is not surprising since the UV source emits along a spectrum; radiation with wavelengths different from that observed with the sensor also contributes in dissociating Cl<sub>2</sub>. The resulting effect is that

the sensor detects a higher transmitted light intensity and the estimated absorption coefficient is effectively lower.

## 2.5 Pre-sensitization/ignition circuitry

Fig. 2.8 is a schematic of the electronic components used to synchronize UV illumination with spark ignition. The sequence of events which ultimately leads to mixture spark ignition is now explained.

- 1. Upon activating the UV lamp, the UV sensor transmits a signal which triggers a positive voltage step generator.
- 2. This positive voltage source in turn activates a delay generator.
- 3. After an amount of time equal to that set on the delay generator, the latter sends a nanosecond pulse to an amplifier which is used to drive the next stage.
- 4. Finally, the amplified pulse is used to activate an EG&G TM-11 trigger module which sends a weak spark (i.e., maximum energy ≈ 10mJ) across the electrodes of the igniter (with a gap fixed at about 3 mm)

A detailed description of the data reduction techniques for the current study is covered in appendix C.



Fig. 2.1 Schematic of detonation tube



Fig. 2.2 Schematic of time-of-arrival (TOA) probes mounted on detonation tube



Fig. 2.3 Enlarged view of optic probe assembly



Fig. 2.4 Overall UV sensing setup



Fig. 2.5 Enlarged view of UV sensor assembly



Fig. 2.6 Cl<sub>2</sub> absorption coefficient as a function of wavelength at room temperature


Fig. 2.7 Transmitted UV light as a function of  $Cl_2$  concentration at  $22^{\circ}C$  (UV sensor calibration data)



Fig. 2.8 Schematic of ignition timing components

## Chapter 3: Results and Discussion

The mixture used throughout the present investigation was  $1.5H_2 + Cl_2$  with an initial temperature of  $T_i = 295$  K and at two initial pressures (i.e.,  $P_i = 4$  and 4.8 kPa). Pre-sensitization of this detonable mixture with atomic Cl free radicals was achieved via UV photolysis before spark ignition. The mixture was first illuminated with UV light for a preset period of time to allow radical buildup, then a flame was initiated and the transition to detonation was determined. Before discussing the results due to free radicals on DDT, control experiments were first performed.

### 3.1 DDT without UV pre-sensitization

Fig. 3.1 shows the steady detonation velocity in the  $H_2/Cl_2$  mixture as a function of initial pressure. Also plotted for comparison are the theoretical Chapman-Jouguet (CJ) values. Additional experimental values for the detonation velocities obtained in a smooth tube of similar diameter are also shown in Fig. 3.1. Due to the presence of the Shchelkin spiral, a high velocity deficit accompanied with fluctuations on the order of 6% are obtained when compared to the results from a smooth tube. For an initial pressure of 4 kPa,  $V_{\text{STEADY}} = 1497$  m/sec, while for 4.8 kPa,  $V_{\text{STEADY}} = 1634$  m/sec as compared to values of about 1790 m/sec for a smooth tube. It should be noted that the data obtained in the smooth tube are slightly higher than the theoretical CJ value for this particular mixture, since the  $H_2/Cl_2$  system belongs to the class of pathological detonations (Duquette [28]).

Figs. 3.2 and 3.3 show the trajectory of the accelerating flame for initial pressures of 4 and 4.8 kPa respectively. Since most of the run-up time is due to the initial laminar flame becoming turbulent, there are some fluctuations associated with the flame acceleration regime and, hence, run-up time. Using the data from these x-t plots, an average flame velocity between probe locations can be calculated. Figs. 3.4 and 3.5 are the corresponding diagrams of reaction front velocity as a function of position from the igniter. A flame was initiated at one of the closed ends (i.e., at x = 0) and accelerated continuously to a value equal to about half the CJ value. As shown in the works of Moen et al. [29], an accelerating turbulent flame can generate pressure waves ahead of itself. These eventually amplify, catch up with one another and may either coalesce to form a shock, or overtake and amplify an already existing weak shock. Either cases can produce the thermodynamic states necessary for the onset of an overdriven detonation. This is observed in Figs. 3.4 and 3.5 when the luminous front accelerates above the steady detonation velocity. Eventually, the detonation slowed down and stabilized at the steady value. The results for both cases show large scatter in the pre-detonation period, which is characteristic of a highly turbulent flame brush. Note that although there appears to be more scatter in the case of Fig. 3.4, one has to keep in mind that this diagram shows the results of more than 30 trials, whereas Fig. 3.5 displays the results of only 10 experiments.

#### 3.2 Photochemical reaction without spark ignition

UV illumination of the mixture at 4 kPa initial pressure results in a slow reaction when atomic Cl radicals are produced. To complete this reaction requires a time typically on the order of 20 secs. The absence of photochemically induced spontaneous explosion is due to the diffusion losses of the Cl radicals to the tube wall at lower pressure. This permits the chain terminating elementary reactions

> $Cl + Cl + Wall \rightarrow Cl_2 + Wall$  $H + H + Wall \rightarrow H_2 + Wall$

to compete effectively against the chain propagating reactions (Rollefson and Burton [15], Kondrat'ev [16], Calvert and Pitts [17], Noyes and Leighton [18], Ellis and Wells [19])

```
Cl + H_2 \rightarrow HCl + HH + Cl_2 \rightarrow HCl + Cl
```

thereby slowing down the overall reaction rate and preventing a runaway explosion. This slow reaction indicates that sufficient time is available to carry out the ignition of this pre-sensitized mixture and observe the DDT process.

For a higher initial pressure of 4.8 kPa, UV illumination eventually leads to photochemical auto-ignition. Since the goal of this study was to investigate the effect of free radicals on the DDT process, spark ignition of the mixture had to be achieved before the onset of this photochemically induced explosion. It was necessary, therefore, to find the delay time required for the mixture to explode following UV irradiation alone. Thus, a series of experiments was carried out in which the mixture was irradiated with UV and the transmitted UV light monitored, to provide a measure of the absorption and hence radicals produced. Fig. 3.6 represents a typical signal of the transmitted UV light intensity as a function of time. After switching on the UV fluorescent tube, a transient period of about 65 msec is required to reach steady light emission. This is followed by an induction period, during which there is a slow build up of Cl free radicals. After a time typically on the order of 200 msec, the mixture undergoes rapid auto-ignition, as indicated by the rapid rise in transmitted UV light intensity. Note that the signal displays a 120 Hz oscillation which is due to the fact that the fluorescent tube is powered by the 60 Hz electric line. A photochemical induction period was defined as the time between when the UV light is switched on, and auto-ignition as indicated by the second abrupt rise in transmitted UV light. By making use of the approximation described in section 2.4.3, data from Fig. 3.6 can provide an approximate measure of the Cl<sub>2</sub> concentration-time history, as shown in Fig. 3.7. The initial concentration is roughly around the theoretical value of 0.78 mol/m<sup>3</sup> and decreases to about 0.45 mol/m<sup>3</sup> right before auto-ignition. The final concentration after explosion is practically 0 mol/m<sup>3</sup>. Assuming a constant volume explosion (i.e., constant internal energy and volume), and the combustion products to be

composed of  $H_2$ ,  $Cl_2$ , HCl, H, and Cl, a thermochemical equilibrium calculation (the STANJAN equilibrium code was used for this) gives

 $1.5 H_2 + Cl_2 \iff 0.146 Cl + 1.854 HCl + 10^4 Cl_2 + 0.0603 H + 0.543 H_2$ 

The measured concentration of  $Cl_2$  at the end of the photochemical reaction, therefore, is in good agreement with the amount calculated from thermochemical equilibrium principles.

To obtain an idea of the reproducibility of the experiment, the results of a number of similar trials are shown in Fig. 3.8. The flame acceleration and DDT in the present apparatus takes between 2 to 4 msec, which is well below any of the measured induction periods due to UV irradiation alone. It is possible, therefore, to ignite the mixture during the photochemical induction period, and observe the effect of free radicals produced in the photodissociation process on DDT. The scatter in the induction time can be explained by the following reasons: first, the reaction rate, and hence induction time, are known to be very sensitive to the presence of trace impurities such as O2 and H2O (Rollefson and Burton [15], Kondrat'ev [16], Calvert and Pitts [17], Noyes and Leighton [18], Ellis and Wells [19] and Patureau, Toong and Garris [25]), the concentrations of which were not determined in the present tests. Secondly, the light intensity from a UV fluorescent black-light tube varies with usage time. Variations in the incident light intensity may therefore produce fluctuations in the photochemical induction times. It was also found that the UV radiation intensity changes slightly along the fluorescent tube and, therefore, may be responsible for creating variations in the radical concentration along the

detonation tube. Since the transmitted UV light was only monitored at the same location for all tests, it is not known whether such a gradient existed or not. If it did, there would result gradients in the photochemical induction time which could influence the scatter.

### 3.3 The effect of free radicals on DDT

Results of the experiments in which photodissociation by UV was used to presensitize the mixture with Cl radicals before spark ignition are now presented. The timetrajectories are shown in Figs. 3.9 and 3.10, while Figs. 3.11 and 3.12 show the corresponding velocity-distance results. The mixture is ignited at x = 0, and the flame again is found to accelerate to a value above the steady detonation velocity, then decays and stabilizes around the steady value. As seen in Fig. 3.11, at an initial pressure of 4 kPa, there does not appear to be any observable effects on DDT whether UV sensitization is employed or not. With an initial pressure of 4.8 kPa, however, onset of detonation is observed to occur about 2 tube diameters earlier, when compared to the case without UV irradiation. In the works of Patureau, Toong and Garris [25], it was found that significant amplification of sound pressure fluctuations can result from the interactions between the acoustics and the kinetics of the reacting mixture. Similarly, in a free radical environment, pressure waves generated by the accelerating flame may amplify at a higher rate such that transition to detonation can occur earlier. This promoting effect is not observed in the case of the mixture at 4 kPa initial pressure, as the concentration of free radicals is measurably too low.

32

A direct comparison between the results due to DDT with and without UV is made for the 4.8 kPa initial pressure. V-x diagrams are shown simultaneously in Fig. 3.13. Instead of plotting all V-x datapoints (as in Figs. 3.5 and 3.12), this figure comprises bands that highlight the average V-x regions with and without UV respectively, thereby providing a more global picture of the results at hand. The shaded envelope shows the results without UV, whereas the transparent envelope represents those results with UV. From the extent of the bands, one can immediately see that results due to UV exhibit more fluctuations and scatter in the detonation regime than those without UV. Furthermore, the detonation velocity of the mixture under UV illumination takes a longer distance to decay to the steady value, namely, about 8 to 10 tube diameters compared with 6 tube diameters for the mixture without UV. With the addition of free radicals, transverse shock waves could be amplified in a manner analogous to the amplification of acoustic waves observed in the experiments by Patureau, Toong and Garris [25]. This may account for the increased fluctuations and the prolonged decay of the overdriven detonation velocity to the steady value.

### 3.4 Lee criterion for self-initiation

Results obtained may also suggest that the introduction of free radicals sensitizes the mixture by accelerating induction kinetics (i.e., reduces the induction time before detonation onset). Lee [1] proposed a criterion to obtain a qualitative estimate of the burning rate defined for self-initiation of a detonation in a given fuel/oxidizer mixture. He proposed a model whereby the critical states for the onset of detonation are obtained via the adiabatic compression of a shock wave generated by the expanding products behind the turbulent flame. The rate of energy release in the turbulent flame brush can be translated to the rate of work done by a piston that produces the required shock strength. The expression is given by

$$\frac{u_t}{C_o} \approx \frac{4(\gamma - 1)M_s^3}{(\gamma + 1)^3 \frac{q}{C_o^2}} \qquad \text{Eq. 3.1}$$

where,

 $u_t$  = turbulent flame speed

 $C_0$  = sound speed ahead of the shock

 $M_S$  = auto-ignition shock Mach number relative to  $C_o$ 

q = chemical energy release per unit mass of reactants across a flame

 $\gamma$  = ratio of specific heats of reactants

The quantity q is calculated as the difference in the enthalpies of formation of the products and the reactants, that is,

$$q = \frac{\sum \Delta H_{f_{PRODUCTS}} - \sum \Delta H_{f_{REACTANTS}}}{total mass of reactants} \quad \text{Eq. 3.2}$$

In the end, one obtains a heat release per unit mass of reactants (note that a negative value of q indicates that the reaction is exothermic). For the onset of detonation, the turbulent flame speed must be such that it could generate a shock of sufficient strength for autoignition. Since  $u_t \propto M_s^3$ , a small decrease in the required shock strength  $M_s$  (due to presensitization) will produce a significant decrease in the turbulent flame speed  $u_t$ . On the other hand, since  $u_t \propto \frac{1}{q}$ , the influence of slightly increasing the heat release is not as strong as decreasing  $M_s$ . Below is a table of the parameters required to compute Eq. 3.1 for the mixture 1.5 H<sub>2</sub> + Cl<sub>2</sub> at 4.8 kPa and 298 K initial conditions (i.e., without presensitization). The STANJAN equilibrium code was used to calculate the heat release per unit mass q across an adiabatic flame (i.e., isobaric heat addition). An overall value of  $\gamma$ 

will be calculated using the frozen sound speed of the reactants (i.e.,  $\gamma = \frac{C_o^2}{R_{reactants}T}$ ) and

the molar mass of the reactants will be denoted by the variable  $\mu$ . The value of  $M_s$  (i.e., the Mach number required to raise the temperature to auto-ignition values) requires knowledge of the reaction kinetics and, for the moment, will be left as an unknown.

$q  (\text{kJ/}_{\text{kg of reactants}})$	Y	$\mu$ (g/mol)	$C_o$ (m/sec)	M <sub>s</sub>	$u_t$ (m/sec)
2134	1.36	29.572	338	?	$1.995 M_s^{3}$

Lee [1] emphasizes that the turbulent burning velocity  $u_t$  is based on the rate of energy release per unit area of the tube, and may be attributed to both large scale flame folding and small scale turbulent effects. Furthermore, this criterion may be a necessary condition for DDT, but it is not sufficient. Lee [1] again points out that since flame folding is a transient process, the shock wave generated as a result of the increase in the rate of energy release is also transient. For detonation onset, the critical states must be maintained for a certain minimum duration in order for auto-ignition to occur. If the shock duration is too short, then the expansion waves associated with shock decay will cool the gases below their auto-ignition limit. This minimum duration should be at least on the order of the induction time corresponding to the auto-ignition temperature.

In the case with UV pre-sensitization, Cl radicals within the reactants produce a different equilibrium concentration of H and HCl products. Consequently, the value of q, as defined by Eq. 3.2, is changed. The parameters required for the calculation of  $u_t$  are given below for a mixture of typically  $1.5H_2 + 0.76Cl_2 + 0.48Cl$  at 4.8 kPa and 298 K initial conditions. This assumes that the amount of  $Cl_2$  dissociated, as measured by the UV sensor, has all been converted into Cl radicals only, which, during the photochemical induction period, constitutes a good approximation.

$q_{uv}  ({\rm kJ/}_{\rm kg \ of \ reactants})$	γιιν	μ (g/mol)	$C_{o_{UV}}$ (m/sec)	M <sub>s<sub>liv</sub></sub>	$u_{t_{\ell N'}}$ (m/sec)
2388	1.40	26.982	358	?	$2.214 M_{s_{th}}^{3}$

Incorporating  $C_o = \sqrt{\gamma \frac{R_{universal}}{\mu}T}$  in Eq. 3.1 will give the ratio of the two turbulent flame

velocities as

$$\frac{u_{t_{UV}}}{u_{t}} \approx \frac{\left(\frac{4(\gamma-1)\gamma^{\frac{3}{2}}}{(\gamma+1)^{3}}\right)_{UV}}{\left(\frac{4(\gamma-1)\gamma^{\frac{3}{2}}}{(\gamma+1)^{3}}\right)} \left(\frac{\mu}{\mu_{UV}}\right)^{\frac{3}{2}} \left(\frac{q}{q_{UV}}\right) \left(\frac{M_{s_{UV}}}{M_{s}}\right)^{3} \qquad \text{Eq. 3.3}$$

Substituting the values from the last two tables gives

$$\frac{u_{t_{UV}}}{u_t} \approx (1.082)(1.147)(0.894) \left(\frac{M_{s_{UV}}}{M_s}\right)^3$$

Note that the three numerical values, corresponding to the influence of changing  $\gamma$ ,  $\mu$  and q respectively, are all on the same order of magnitude. Simplifying further

$$\frac{u_{t_{UV}}}{u_t} \approx (1.11) \left(\frac{M_{s_{UV}}}{M_s}\right)^3 \qquad \text{Eq. 3.4}$$

The numerical value, therefore, incorporates the effect of changing the thermodynamics  $(\lambda \text{ and } \mu)$  and the energetics (q). Note that the influence of the auto-ignition shock Mach number  $M_S$  becomes greater than the effect of changing either the energetics or the thermodynamics of the mixture when

$$(1.11)\left(\frac{M_{s_{UV}}}{M_s}\right)^3 < 1$$

or

$$\frac{M_{s_{tiv}}}{M_s} < \text{about } 0.97$$

Thus, a decrease in the auto-ignition shock Mach number  $M_s$  of more than only 3% will give rise to a reduction in the required turbulent flame velocity  $u_t$  for DDT. Further reductions in  $M_s$  will produce much more significant reductions in  $u_t$  due to the cubic dependence on  $M_s$ .

In summary, it appears that for both cases of initial pressures studied, sensitization with free radicals of a mixture devoid of chain branching elementary reactions does not seem to produce any significant change in the pre-detonation region. This supports the view that flame acceleration in the pre-detonation regime is mostly dominated by the turbulence (Lee [1]) produced by the obstacles. It is believed that the presence of free radicals in the unburned mixture contributes little to the flame propagation mechanism which is governed by molecular and turbulent transport. Nevertheless, during the early stages of the flame propagation near the igniter, the contribution from turbulence is negligible. Consequently, in this region, the impact of free radicals on the burning velocity may be important. Even though this may affect the flame over a short distance, the time can be significant because of the initially slow flame velocity. It is not clear, however, how this will affect the overall DDT process. The effect of free radical seeding seems to be confined to the period of detonation onset. It is believed that the promoting mechanism is one of higher pressure wave amplification rate, and a reduction in the autoignition induction time (or equivalently, a reduction in the auto-ignition Mach number).



Fig. 3.1 Detonation velocity data in 1.5 H<sub>2</sub> + Cl<sub>2</sub> mixtures at 295 K initial temperature



Fig. 3.2 x-t diagrams of DDT in  $1.5 H_2 + Cl_2$  mixtures at 4 kPa and 295 K initial conditions



Fig. 3.3 x-t diagrams of DDT in 1.5  $H_2$  +  $Cl_2$  mixtures at 4.8 kPa and 295 K initial conditions



Fig. 3.4 *V-x* diagrams of DDT in  $1.5 H_2 + Cl_2$  mixtures at 4 kPa and 295 K initial conditions



Fig. 3.5 *V-x* diagrams of DDT in  $1.5 H_2 + Cl_2$  mixtures at 4.8 kPa and 295 K initial conditions



Fig. 3.6 Typical transmitted UV light data for  $1.5 H_2 + Cl_2$  mixtures at 4.8 kPa and 295 K initial conditions



Fig. 3.7 Typical  $Cl_2$  concentration data for  $1.5 H_2 + Cl_2$ mixtures at 4.8 kPa and 295 K initial conditions



Fig. 3.8 Photochemical induction time data for  $1.5 H_2 + Cl_2$ mixtures at 4.8 kPa and 295 K initial conditions



Fig. 3.9 x-t diagrams of DDT in 1.5 H<sub>2</sub> + Cl<sub>2</sub> mixtures at 4 kPa and 295 K initial conditions with UV pre-sensitization



Fig. 3.10 x-t diagrams of DDT in 1.5 H<sub>2</sub> + Cl<sub>2</sub> mixtures at 4.8 kPa and 295 K initial conditions with UV pre-sensitization



Fig. 3.11 *V-x* diagrams of DDT in 1.5 H<sub>2</sub> + Cl<sub>2</sub> mixtures at 4 kPa and 295 K initial conditions with UV pre-sensitization



Fig. 3.12 *V-x* diagrams of DDT in  $1.5 H_2 + Cl_2$  mixtures at 4.8 kPa and 295 K initial conditions with UV pre-sensitization



Fig. 3.13 Comparative V-x diagrams demonstrating the effect of UV pre-sensitization for  $1.5 H_2 + Cl_2$  mixtures at 4.8 kPa and 295 K initial conditions

### Chapter 4: Conclusions

The results obtained in this study show that the presence of free radicals before ignition promotes DDT by reducing both the run-up distance and the run-up time. Although the influence of free radicals on the transition from deflagration to detonation (DDT) has been confirmed, there appears to be no observable effect on the pre-detonation regime.

The run-up length was reduced from about 10.5 to 8.5 tube diameters, while the run-up time decreased from 2.3 to 2 msec. It was also observed that the initial acceleration of the slow flame up to approximately  $60\% V_{CJ}$  is not influenced by the presence of free radicals. This observation agrees with the generally accepted view that local conditions of turbulence mostly govern the flame acceleration process. On the other hand, the presence of free radicals promoted the final acceleration of the front up to detonation velocities.

The introduction of chain initiating radicals sensitizes the mixture by decreasing the induction time associated with the overall reaction rate. As a result, auto-ignition due to shock compression ahead of the flame is facilitated. Even if sensitization does not produce any change in the flame acceleration regime, a shorter DDT process is anticipated. This agrees with the qualitative criterion by Lee [1], in which the minimum turbulent burning rate required for shock induced auto-ignition ahead of the flame is strongly dependent upon the induction kinetics of the mixture. According to this model, radical sensitization reduces the minimum turbulent burning rate for auto-ignition.

Pressure waves are continuously generated by the accelerating turbulent flame before DDT. It is suspected that free radical seeding increases the rate of pressure wave amplification, thereby accelerating the attainment of auto-ignition temperatures. This could also contribute in promoting DDT.

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# Appendix A: Modification of ballast circuitry

### A.1 Working principle of fluorescent tube

Fluorescent tubes are equipped with a filament at each end, which acts as an electron emitter or cathode. A voltage of about 4 Vrms (referred to as "cathode voltage") is applied across each of these filaments to raise their temperature to sufficiently high levels (i.e., typically about 900 C), so that electrons can be produced through "boil off" (i.e., in a manner similar to that within the electron gun of cathode ray tubes). The lamp also requires a higher potential of about 200 Vrms between the two electrodes across the tube (this is called arc voltage and could be higher depending on the model). This potential difference accelerates the electrons and causes them to collide with atoms of a gaseous element (typically mercury vapor) present in the tube. As a result of the collisions, many atoms are raised to higher energy states. When the excited atoms drop back to their normal level (i.e., ground state), radiation in the ultraviolet range (specifically 253.7 nm for mercury) is emitted and strikes a phosphor coated screen (usually the inner surface of the glass tube). As the screen absorbs this radiation, it emits light of a higher wavelength by means of fluorescence. Different phosphors on the screen emit at different wavelengths; the light source utilized in the current investigation emits radiation in the near UV (i.e.,  $\approx$  300-400 nm) as well as in the visible violet-blue region (i.e.,  $\approx 400-490$  nm) of the electromagnetic spectrum (Serway [30]).

There are two types of Black Light fluorescent lamps, namely, Black Light (BL) and Black Light Blue (BLB). The BL lamps are similar in appearance to standard fluorescent lamps; in addition to near UV, they also produce a certain amount of visible "bluish" light. BLB lamps, on the other hand, have their tubes made of a special deep blue glass filter that absorbs nearly all the visible light but transmits ultraviolet. The UV source used in the current investigation was of the BL type.

### A.2 Working principle of ballast

A fluorescent lamp ballast is an electric transformer. Fluorescent lamps require different voltages during start-up compared to that during steady operation. The role of the ballast is threefold: first, it transforms the 120 VAC line voltage to the requirements of the arc and cathode voltages. Second, the fluorescent tube is seeded with an inert gas additive (e.g., neon, argon,...) such that when it ionizes, the resistance across the lamp decreases. From Ohm's law, as the resistance approaches zero, the current increases without control. Without a device to limit the current, the cathode filaments would burn up at once. The ballast, therefore, limits the current which the lamp can draw. Thirdly, the ballast also serves the purpose of controlling power consumption by including a suitable RC circuit to adjust for the phase difference between voltage and current.

### A.3 Ballast circuitry and modification

Fig. A.1 illustrates the basic electric circuitry for the ballast/fluorescent tube combination. Although both arc and cathode voltages are applied simultaneously, bringing the electrodes to working temperatures can last for periods on the order of a few

59

seconds, which is why such lamps require a corresponding amount of time to reach steady light emission. An alteration was therefore necessary to de-couple both voltage applying stages. Namely, the user would first apply the cathode voltage in order to "warm up" the electrodes without turning on the lamp and, after a few seconds, apply the larger arc voltage across the tube to turn on the lamp. Such a modification is shown in Fig. A.2, and was found to reduce the overall start-up time from a few seconds down to about 45 msec.


Fig. A.1 Electric circuitry of fluorescent tube ballast



Fig. A.2 Schematic of ballast modification

# Appendix B: Optical probe response

### **B.1** Phototransistor response

OP505 phototransistors are inadequate during the early stages of the flame acceleration process. Fig. B.1 shows a typical OP505 signal. Light intensity measurements are highly qualitative and therefore the y-axis is left without units. This procedure will be followed for all TOA probe traces shown in this document. Spark ignition is indicated by a sharp rise, and is followed by a long "RC" like decay which lasts for periods in excess of 2.4 msec. It appears that this time constant is due to the intrinsic capacitance of transistor junctions. Onset of detonation often occurred within this time frame and, as a result, OP505 sensors could not be used to observe DDT. They were, however, suitable for time of arrival measurements when positioned sufficiently far from the igniter. PIN photodiodes are devoid of this problem and, hence, were used to monitor the DDT region. The basic electronic circuitry for either probes consisted in a current to voltage converter.

## B.2 Relative probe response

In order to verify the response of both probes relative to one other, a number of trials were performed whereby both sensors were located at the same cross-section. Fig. B.2 shows a sample trace of such a test. In this case, both sensors were monitoring an established detonation. One can see that although the OP505 has a much slower rise time (if we define this as the time for the signal to reach its first local peak), both sensor

signals have a coinciding start of rise; this is the portion of the signal which was used for time-of-arrival measurements.



Fig. B.1 Typical OP505 phototransistor signal monitoring detonation in a mixture of  $1.5 H_2 + Cl_2$  at 4.8 kPa and 295 K initial conditions



Fig. B.2 Comparative traces showing signal start-of-rise of both phototransistor and PIN photodiode located at the same distance from the igniter (both probes are monitoring detonation in a mixture of  $1.5 \text{ H}_2 + \text{Cl}_2$  at 4.8 kPa and 295 K initial conditions)

# Appendix C: Data reduction

While estimating the average velocity of fully established detonations with luminosity probes is a fairly straightforward task, inferring the point of transition from their signals when a mixture undergoes DDT is not so obvious. In the pre-detonation region, where the turbulent flame takes the shape of a distorted luminous front, measurements of the arrival time are often highly subject to interpretation, if not impossible. Nevertheless, it is still possible to define some parameters which may at least give an indication of the influence of free radicals on DDT. Also of interest are parameters characterizing the photochemical processes which take place when the mixture is exposed to UV radiation. Following are the description of these parameters, and how they are obtained from experimental data.

#### C.1 Time-of-arrival (TOA)

The reaction front time of arrival (TOA) is the basic measurement from which velocities and DDT characteristic parameters are calculated. It is obtained by measuring the time at which a probe "sees first light". On the oscilloscope, this translates into measuring the time when the luminosity probe signal starts rising above local noise levels. The rise time was defined as the time required for the signal to reach its first local peak. Typical signals from 5 PIN probes monitoring DDT are shown in Fig. C.1. In the pre-detonation region (probes 1, 2 and 3), luminosity signals have very slow rise times, typically hundreds of microseconds, and only approximate times indicating the presence

of a turbulent flame can be estimated. Consequently, it is expected that calculated predetonation velocities will suffer large fluctuations. During detonation onset, optic probes give much shorter rise times, typically on the order of 20-30 microseconds (probes 4 and 5). While this period may be viewed as slow for a detonation, scattered light accounts for most of this rise time. Fig. C.2 shows the geometric probe view angle as imposed by the setup. Light within the glass tube diffracts past a 3.1 mm Pyrex glass wall, and emerges within the hollowed out black Delrin cylinder which holds the optic sensing device (i.e., either the OP505 phototransistor or the fiber optic cable). The light capture angle  $(\approx 7.85^{\circ})$  is such that the base of the cone of visibility is about 10.5 mm wide (neglecting both curvature and index of refraction of the Pyrex tube wall). Detonation velocities in H<sub>2</sub>/Cl<sub>2</sub> are typically between 1.5-2 mm/µsec, so the minimum time required for a planar detonation to traverse half the cone is about 2.6-3.5 µsec. Though this is still less than the typical 20-30 µsec mentioned earlier, another factor which increases signal rise time is due to the fact that the inner surface of the black Delrin cylinders was not perfectly opaque. Consequently, as shown in Fig. C.3, light reflections along these inner walls further increases the probe view angle. Roughening this surface with abrasive cord or the use of thin 40 cm long steel light pipes failed to produce any reduction in the signal rise time.

# C.2 Average reaction front velocity (V<sub>average</sub>)

An average reaction front velocity was calculated based on the time-of-arrival measurements made at known locations along the tube, namely,

$$V = \frac{\Delta x}{\Delta t}$$

where  $\Delta x$  and  $\Delta t$  are the differences between probe locations and arrival times respectively. This velocity is then plotted as a function of the mid-point between probes from which the velocities were calculated.

# C.3 Characteristic run-up length ( $x^*$ and $x^*_{UV}$ )

If one restricts the field of view to a thin slit along the length of the glass tube in a manner analogous to streak photography, then Fig. C.4 shows what a typical streak photo of DDT would look like. It is a diagram of the average reaction front position from the igniter as a function of time (i.e., an x-t plot). The run-up length is defined as the distance from the igniter where detonation onset occurs. Unfortunately, for the mixture under consideration, streak photography was ineffective. A time-trajectory plot could only be inferred with the use of optic probes discretely located along the glass detonation chamber. This point raises an important issue which warrants discussion: the choice of an adequate TOA probe spacing. Probes located too far apart will be completely blind to the process of DDT. On the other hand, while a closer spacing will increase the sensitivity to fluctuations, this configuration is now vulnerable to multidimensional effects. Onset of detonation in obstacle laden tubes often manifests itself as a localized explosion within the turbulent flame brush, where it develops into a hemispherical detonation. If probes are too closely spaced, the hemispherical luminous front may reach multiple probes almost simultaneously, such that a calculation of the average velocity based on TOA measurements would yield enormous values. This is simply a phase

velocity due an event reaching two sensors almost at the same time, and does not represent the velocity of detonation. Experience showed that a probe spacing of 2 tube diameters always produced sequential signals and realistic average velocities.

As shown in Fig. C.5, two scenarios of detonation onset within an obstacle laden tube are possible. In case a), detonation initiated close to probe 2. The average velocity between probes 1 and 2 will be below detonation speeds ( $V_{low}$ ), while that between probes 2 and 3 will indicate a high velocity ( $V_{high}$ ), possibly greater than the Chapman-Jouget value, which is typical of an overdriven detonation formed during onset. In this case, since most of the velocity ( $V_{high}$ ) is due to detonation, locating the run-up position at probe 2 is a good approximation. A different situation arises in scenario b), namely, onset occurred somewhere between probes 1 and 2 such that the measured velocity is now close to the steady detonation velocity (possibly lower than  $V_{CI}$  because of obstacles in the tube). In this case, the run-up length is said to be located midpoint between probes 1 and 2. As one can see, within the limitations of the current setup, this parameter cannot be estimated with greater accuracy. Since onset of detonation occurs in a very localized region, the distance required for the event to fill the entire tube cross section is on the order of 1 tube diameter. The error in estimating run-up length, therefore, is at best no less than 1 tube diameter.

## C.4 Characteristic run-up time (t\* and t $_{UV}$ )

Referring back to Fig. C.4 again, a run-up time t\* is defined as the intersection of the time axis with a line extrapolated from the linear fit of the datapoints obtained in the

detonation region. This measurement is both easier to obtain and independent from the characteristic run-up length discussed in the previous section. It therefore constitutes a redundant measurement to detect the effect of radicals on DDT. Note, however, that calculation of this parameter is not a sufficient condition to completely characterize the effect of free radicals on DDT. Fig. C.6 shows several scenarios for the same run-up time due to radicals. Since free radicals which would otherwise be produced thermally during an un-sensitized experiment are now present in the mixture, a decrease in the induction time associated with the period of detonation onset is expected. This means that cases d) and e) are unlikely to occur. Now the question remains as to what will be the effect on the pre-detonation laminar and turbulent deflagration regimes. Scenario a) implies that the effect inhibits flame propagation but promotes detonation formation. Scenario b) shows that the effect is confined to the period of detonation onset, while scenario c) shows that radicals both promote flame propagation and onset of detonation. If one regards the expanding products behind the advancing flame as a driving force that generates shock waves within the unburned reactants, a faster flame will drive stronger shocks. A stronger shock, in turn, will create higher temperatures thereby lowering the induction time associated with shock induced auto-ignition. Thus, a slower flame is not expected to undergo "earlier DDT", such that case a) is not possible. Cases b) and c), therefore, appear to be the only plausible outcomes.

## C.5 Photochemical explosion time (t<sub>induction</sub>)

In the case of the mixture at 4.8 kPa initial pressure, UV illumination will, after a certain time, cause the reactants to auto-ignite and undergo thermal explosion. Since the

goal of the present study was to investigate the effect of photochemically generated radicals on DDT, it was necessary to gain knowledge of the induction time to photochemical explosion. Fig. C.7 shows a typical trace of transmitted UV light. An induction period was defined as the time between the activation of the UV lamp and auto-ignition of the mixture indicated by a rapid rise in the UV sensor signal.



Fig. C.1 Typical PIN photodiode traces showing DDT in a mixture of  $1.5 H_2 + Cl_2$  at 4.8 kPa and 295 K initial conditions



Fig. C.2 Optic probe view angle schematic



Fig. C.3 Effect of scattered light on optic probe view angle



Fig. C.4 Features of the x-t diagram



a)

b)

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Fig. C.6 Scenarios involving same run-up time but different run-up lengths



Fig. C.7 Typical transmitted UV light signal to get photochemical induction time ( $t_{induction}$ ) before auto-ignition and thermal explosion in a mixture of 1.5 H<sub>2</sub> + Cl<sub>2</sub> at 4.8 kPa and 295 K initial conditions