Hydrogen Peroxide Thermal Decomposition: new Features

[1]Nabiha Chaumeix, [1]Servane Pichon, [2]Laurent Catoire, [1]Claude Paillard

[1] ICARE-CNRS and University of Orléans

1C, avenue de la Recherche Scientifique
45071 Orléans Cedex 2, France

[2] ENSTA ParisTech

32, boulevard Victor
75739 Paris Cedex 15, France

1 Introduction

Hydrogen peroxide is an endothermic compound, i.e. it has a positive formation enthalpy and is therefore able to decompose exothermically and to sustain a decomposition flame. This interesting feature is the cause of the use of H_2O_2 in space propulsion as a monopropellant which is decomposed on a heated catalytic bed. Moreover, in the frame of the energetic and environmental issues, hydrogen peroxide can be considered as a "green" propellant since its decomposition products are water and O_2, minimizing harmful effects on our environment. Hydrogen peroxide, once mixed with water, presents many advantages, such as safety of use, easy handling, convenient storage characteristics (for more than one year at ambient condition), high density and high boiling point. Based on these properties, and the fact that many steps in its decomposition are not known, new studies are required in order to discuss its high-temperature chemistry. Since H_2O_2 is only available as a solution with water, it is important to take into account water vapor during its decomposition. Numerous previous studies are reported in the literature. Hydrogen peroxide thermal decomposition was studied in flow reactors [1-3], in static reactors [4] or in shock tubes [5-9] at temperature between 750 and 1680 K. Shock tube studies allowed to determine rate constants of four important reactions, noted hereafter R1, R2, R3 and R4, for H_2O_2 thermal decomposition: $H_2O_2 + M = 2OH + M$ (R1), $H_2O_2 + OH = H_2O + HO_2$ (R2), $HO_2 + HO_2 = H_2O_2 + O_2$ (R3) and $OH + HO_2 = H_2O + O_2$ (R4). These studies were needed for the development of H_2O_2 detailed chemical kinetic models. H_2O_2 kinetic model is a sub-mechanism of H_2+O_2 and vice-versa. A further validation of the H_2O_2 model will enhance the predictions of the H_2/O_2 mechanism for which a great amount of work has been devoted [10-19].

Correspondence to: chaumeix@cnrs-orleans.fr

This work is composed into two sections: experiments and modeling. First, we studied experimentally the auto-ignition delay times of $H_2/O_2/Ar$ mixture and the decomposition times of $H_2O_2/H_2O/Ar$ mixture. Then experimental times were compared to predicted times in order to discuss H_2O_2 combustion chemistry. It appears that the kinetics of excited OH radicals, hereafter noted OH*, needs to be considered. This last part of the work is not presented in this extended abstract.

2 Experimental Setup

The experiments were performed using a glass shock tube in order to prevent adsorption and premature decomposition of H_2O_2. The tube (i.d. 50 mm) has a 2-m-long driver section filled with helium (at pressure P_4) and a test section about 9 m long, in which the test mixtures are introduced at ambient temperature T_1 and total pressure P_1. Several diagnostic instruments are located in the second half of the driven section: four piezoelectric pressure transducers, mounted flush with the inside wall, for shock wave velocity measurements and a calcium fluoride optical windows pair mounted at 10 mm from the tube end, associated with a 306 nm filter equipped with a Hamamatsu photo-multiplyer R928, for following OH emission at 306 nm from which the decomposition characteristic time ($\tau_{100\%}$ or $\tau_{50\%)}$ is deduced. The characteristic time τ is determined between the onset of the incident shock wave and the time of maximum of the excited OH emission peak for $\tau_{100\%}$ or the time of the half of the maximum of the peak emission for $\tau_{50\%}$ (**Figure 1**). Gaseous mixtures are prepared by the partial pressure method at ambient temperature. All the hydrogen peroxide solution (70%w/w H_2O_2 – 30%w/w H_2O) injected in the experimental setup is vaporized in spherical glass vessel and diluted with argon in order to prevent preferential vaporization. Due to the low level of the emission signal, the uncertainty on τ is around 30%.

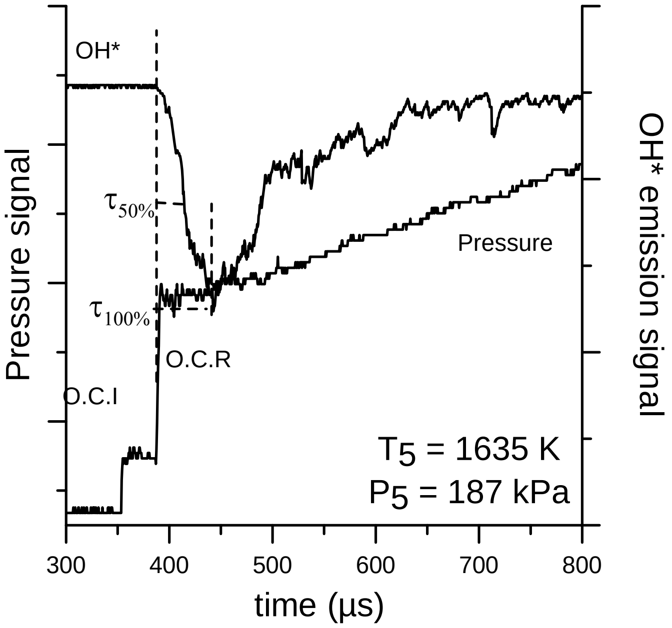

Figure 1. Simultaneous record of OH* emission signal and pressure signal, Mixture : 0.5 mol% {HP+water} + 99.5 mol%Ar ; $\tau_{100\%}$=55 µs and $\tau_{50\%}$=29 µs.

3 Experimental results: $H_2/O_2/Ar$ ignition delays

Since H_2O_2 decomposition kinetics is a sub-mechanism of H_2/O_2 system, one has to find the best mechanism for hydrogen oxidation to be used for the decomposition study of hydrogen peroxide. In order to select the appropriate model among the detailed kinetic mechanisms presented in the recent litterature, a series of experiments on $H_2/O_2/Ar$ ignition delay times have been conducted in this work. Ignition delay times have been measured from OH* emission at 306 nm for different H_2/O_2 mixtures highly diluted in argon (99 mol%). Three different equivalence ratios were investigated (0.4- 0.75-1) for reflected shock temperature ranging between 1164 K and 1520 K and for reflected shock pressure around 215 kPa. Ignition delay times was determined at the maximum ($\tau_{100\%}$) and at the half ($\tau_{50\%}$) of OH* excited emission peak. Figure 2a and 2b show the evolution of the auto-ignition delay times versus the temperature inverse. As expected, the ignition delays decrease when the temperature increases and when the concentration in oxygen increases. The same behavior is observed no matter what definition for the ignition delay time is adopted ($\tau_{100\%}$ in figure 2a and $\tau_{50\%}$ in figure 2b).

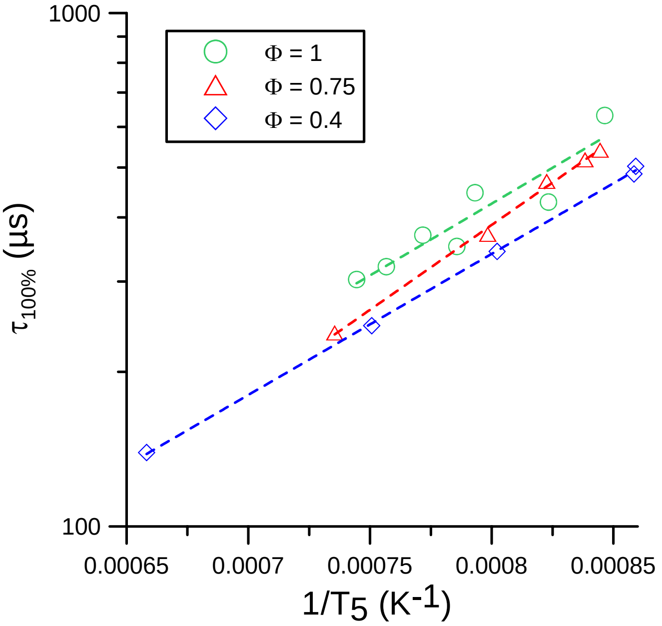

Figure 2a. Shock-tube ignition delay times ($\tau_{100\%}$) of H_2/O_2 in 99% of argon at equivalence ratios 0.4-0.75 and 1.

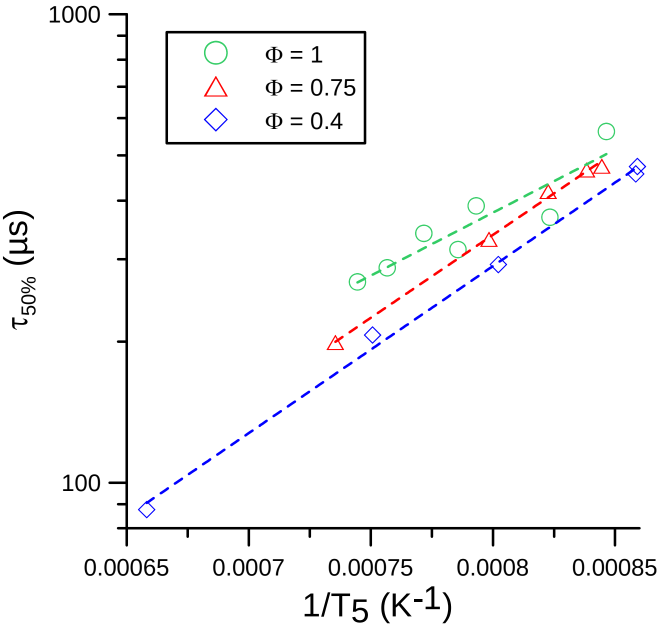

Figure 2b. Shock-tube ignition delay times ($\tau_{50\%}$) of H_2/O_2 in 99% of argon at equivalence ratios 0.4-0.75 and 1.

4 Experimental results: $H_2O_2/H_2O/Ar$ induction times

H_2O_2 decomposition characteristic time τ for two different mixtures (
Table 1) was determined in a temperature range 1260-1700 K and a pressure range 150-230 kPa. H_2O_2 amount in mixtures is 0.28 or 0.55 mol%. Experimental results $\tau_{100\%}$ and $\tau_{50\%}$ are given in Figure 3. Whatever the definition adopted for the determination of τ, induction times decrease when temperature increases. When the H_2O_2 initial concentration in the mixture is increased by a factor of 2, a decrease of τ by about a factor of 4 is observed.

Table 1: $H_2O_2/H_2O/Ar$ mixtures studied in this work.

	Mol% H_2O_2	Mol% H_2O	Mol% Ar	Temperature range, K	Pressure range, kPa
Mixture 1	0.5527	0.4473	99	1260 - 1650	150 - 230
Mixture 2	0.27635	0.23365	99.5	1260 – 1700	170 – 230

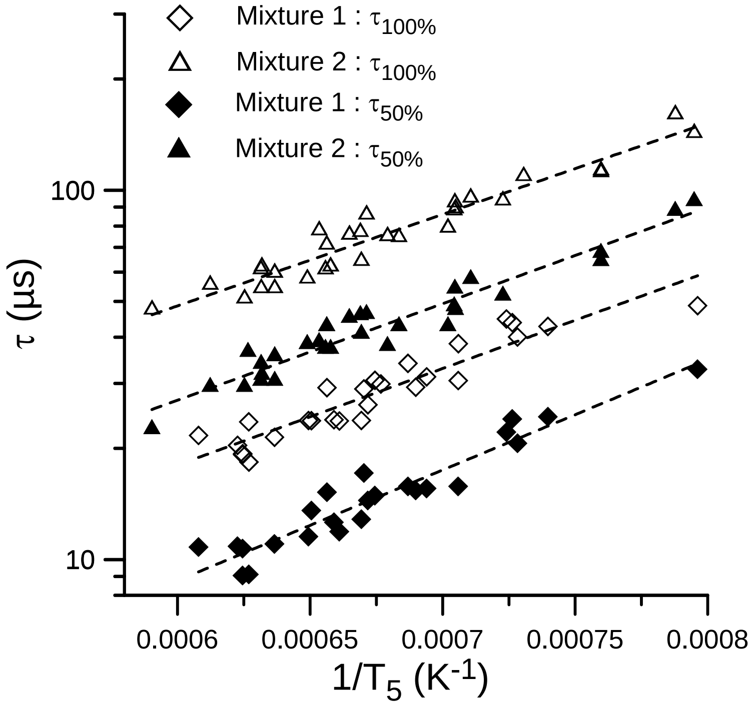

Figure 3. Hydrogen peroxide decomposition characteristic times (τ) for the two different mixtures given in the Table **1**, determined from the maximum OH* emission peak ($\tau_{100\%}$) or from the half OH* emission peak ($\tau_{50\%}$). Dashed lines represent best linear fit of experimental data.

Although scientifically meaningless nowadays, but still interesting for engineering purposes, characteristic times τ can be expressed by least-squares multiregression, without constraint, as:

$$\tau = A \times [H_2O_2]^{\alpha} \times [H_2O]^{\beta} \times [Ar]^{\gamma} \times e^{\frac{+Ea}{RT}}$$

and because H_2O concentration is proportional to H_2O_2 concentration and γ is equal to zero because of the high dilution in Ar then τ can be expressed as

$$\tau = A' \times [H_2O_2]^{\alpha+\beta} \times e^{\frac{+Ea}{RT}}$$

Data reported in Fig. 3 lead to the following relationships:

$$\tau_{100\%}\,(s) = 1.44\times10^{-11} \times [H_2O_2]^{-1.38} \times e^{\frac{+8622}{T}}$$

and

$$\tau_{50\%}\,(s) = 6.11\times10^{-13} \times [H_2O_2]^{-1.51} \times e^{\frac{+9431}{T}}$$

Much more interesting is the kinetic interpretation of these experimental data which cannot be developed here thoroughly due to space limitations.

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