

# On the rate constants of $\text{OH} + \text{HO}_2$ and $\text{HO}_2 + \text{HO}_2$ : A comprehensive study of $\text{H}_2\text{O}_2$ thermal decomposition using multi-species laser absorption

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## Abstract

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and hydroperoxy ( $\text{HO}_2$ ) reactions present in the  $\text{H}_2\text{O}_2$  thermal decomposition system are important in combustion kinetics.  $\text{H}_2\text{O}_2$  thermal decomposition has been studied behind reflected shock waves using  $\text{H}_2\text{O}$  and  $\text{OH}$  diagnostics in previous studies (Hong et al. (2009) [9] and Hong et al. (2010) [6,8]) to determine the rate constants of two major reactions:  $\text{H}_2\text{O}_2 + \text{M} \rightarrow 2\text{OH} + \text{M}$  ( $k_1$ ) and  $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$  ( $k_2$ ). With the addition of a third diagnostic for  $\text{HO}_2$  at 227 nm, the  $\text{H}_2\text{O}_2$  thermal decomposition system can be comprehensively characterized for the first time. Specifically, the rate constants of two remaining major reactions in the system,  $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$  ( $k_3$ ) and  $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$  ( $k_4$ ) can be determined with high-fidelity.

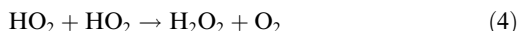
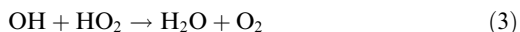
No strong temperature dependency was found between 1072 and 1283 K for the rate constant of  $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ , which can be expressed by the combination of two Arrhenius forms:  $k_3 = 7.0 \times 10^{12} \exp(550/T) + 4.5 \times 10^{14} \exp(-5500/T)$  [ $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ ]. The rate constants of reaction  $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$  determined agree very well with those reported by Kappel et al. (2002) [5]; the recommendation therefore remains unchanged:  $k_4 = 1.0 \times 10^{14} \exp(-5556/T) + 1.9 \times 10^{11} \exp(709/T)$  [ $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ ]. All the tests were performed near 1.7 atm.

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## 1. Introduction

Despite its simplicity, the  $\text{H}_2\text{O}_2$  thermal decomposition system features some of the most important elementary reactions for describing combustion kinetics, particularly reactions involv-

ing perhydroxyl radical. Although the system can be described by only a handful of reactions



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and just four hydrogen-containing species ( $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{OH}$ ,  $\text{HO}_2$ ), these reactions and species are not well characterized. As well, the UV absorption cross-sections of  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$  at temperatures above 1000 K were only measured by one group more than 20 years ago and their values are, to some degree, tied to kinetic interpretation [1–3].

In addition to the uncertainty in the  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$  absorption cross-section data, the rate constants of some of these aforementioned reactions are still subject to large uncertainties. For example, the studies by Hippler et al. [4] and Kappel et al. [5] suggest a strong temperature dependence of the rate constant of Reaction (3) ( $k_3$ ) with a narrow rate constant minimum near 1250 K or 1000 K, respectively. In contrast, recent studies by Hong et al. [6] and Srinivasan et al. [7] show no evidence of such strong temperature dependence of  $k_3$  near 1000 K. However, results reported by Hong et al. [6] were obtained at temperatures higher than 1600 K, which could not directly resolve the possible discrepancy near 1000 K. Furthermore, Reaction (3) was only of secondary importance in the reacting system investigated by Srinivasan et al. [7]; hence scatter in the inferred  $k_3$  values prohibit a definite conclusion regarding  $k_3$  temperature dependency near 1000 K.

Similar to  $k_3$ , the rate constant  $k_4$  of Reaction (4),  $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ , may require a re-evaluation, as most available experimental data at combustion temperatures were obtained by studying the  $\text{H}_2\text{O}_2$  thermal decomposition system [1,3,5], with the exception of one study [3] that also investigated  $(\text{CH}_3\text{O})_2/\text{O}_2$  mixtures. In a closely correlated reacting system such as the  $\text{H}_2\text{O}_2$  thermal decomposition system, once  $k_3$  can be determined with better accuracy, an improved understanding of  $k_4$  naturally follows. In addition, recent updates in the rate constants of Reactions (1), (2), and (5) [8,9,11] can help to reduce the uncertainty in the re-evaluated  $k_4$  values.

Recent advances in laser diagnostics [10] have, for the first time, paved the way to gain comprehensive understanding of the  $\text{H}_2\text{O}_2$  thermal decomposition system by experimentation. In 2010, Hong et al. [9] introduced a sensitive  $\text{H}_2\text{O}$  diagnostic based on tunable diode laser absorption near 2.5  $\mu\text{m}$  to study  $\text{H}_2\text{O}_2$  thermal decomposition behind reflected shock waves. Shortly afterwards, an OH absorption diagnostic near 308 nm was combined with the  $\text{H}_2\text{O}$  diagnostic to investigate  $\text{H}_2\text{O}_2$  pyrolysis in a shock tube [8]. As there are only four hydrogenous species in the reacting system, a diagnostic for a third hydrogen-containing species,  $\text{HO}_2$ , together with conservation of hydrogen, should completely determine the system. Therefore, the goal of the current work is to perform a comprehensive study of  $\text{H}_2\text{O}_2$  pyrolysis by measuring the time-histories of  $\text{H}_2\text{O}$ ,  $\text{OH}$ , and  $\text{HO}_2$  species simultaneously.

## 2. Experimental setup

$\text{H}_2\text{O}_2$  thermal decomposition experiments were performed in a shock tube behind reflected shock waves. The stainless-steel shock tube consists of a 3.7 m driver section and a 10 m driven section, both of which have an inner diameter of 15.2 cm. Temperatures and pressures in the post-shock region were determined from the incident shock speed at the endwall using standard normal shock relations. The incident shock speed was measured using a series of piezoelectric pressure transducers over the last 1.5 m of the shock tube and linearly extrapolated to the endwall. The shock tube was equipped with a turbo-molecular pump that is capable of obtaining an ultimate pressure below  $10^{-6}$  torr, with a leak and outgassing rate of  $\sim 3 \times 10^{-6}$  torr/min.

Laser diagnostics for three species ( $\text{H}_2\text{O}$ ,  $\text{OH}$ , and  $\text{HO}_2$ ) were simultaneously used to study  $\text{H}_2\text{O}_2$  decomposition behind reflected shock waves. All three laser beams were passed across the diameter of the shock tube at a location 2 cm from the shock tube endwall and were in the same axial plane for easy synchronization.

$\text{H}_2\text{O}$  and OH time-histories were measured using a tunable diode laser near 2.5  $\mu\text{m}$  and a ring-dye laser near 308 nm, respectively. These two diagnostics have been successfully utilized in previous  $\text{H}_2\text{O}_2$  pyrolysis studies [6,8,9]; only brief descriptions are provided in this paper. A distributed feedback (DFB) diode laser from Nanoplus GmbH was used to access a strong  $\text{H}_2\text{O}$  absorption transition at 2550.96 nm ( $3920.09 \text{ cm}^{-1}$ ) within the  $\text{H}_2\text{O}$   $v_3$  fundamental vibrational band. The transmitted laser intensity after  $\text{H}_2\text{O}$  absorption was detected by a liquid nitrogen-cooled InSb detector. For the OH diagnostic, the  $\text{R}_1(5)$  line of the  $\text{A}^2\Sigma^+ - \text{X}^2\Pi$  (0,0) band near 306.7 nm was chosen. 1–2 mW of UV light at 306.7 nm was generated at a temperature-tuned AD\*A crystal by doubling the frequency of visible light at 613.4 nm, in a Spectra-Physics 380 ring-dye laser operating with Rhodamine R6G dye. The ring-dye laser was pumped by a 5 W Coherent Verdi cw laser operating at 532 nm. The absorption coefficient of the OH radical is well-established, and measured OH concentrations are accurate to better than  $\pm 5\%$ .

The third wavelength at 227 nm was generated by quadrupling the frequency of the output from a Ti:Sapphire laser.  $\text{HO}_2$  has a strong broadband absorption feature at deep UV wavelengths (210–250 nm) at temperatures ranging from room temperature to 1100 K [1–3,12]. The detection wavelength was chosen based on previous studies which suggest that the  $\text{HO}_2$  absorption cross-section only weakly depends on temperature near this wavelength [2,3]. The Ti:Sapphire laser (MIRA HP, Coherent Inc.) was operated at a repetition rate of approximately 76 MHz (pulse

duration  $\sim 2$  ps) between 700 and 980 nm with a peak output of 1 watt and a Gaussian spectral profile (FWHM  $\sim 1$  nm). The near infrared output from the Ti:Sapphire laser was converted into UV light between 211 and 235 nm with a fourth harmonic generator (FHG, Coherent Inc.). Two silicon detectors with a bandwidth of 1 MHz (Newport 2032) were used to measure the intensities of both the reference beam ( $I_0$ ) and the transmitted beam ( $I$ ). The method has been previously used to investigate  $O_2$  absorption cross-section at temperatures above 1100 K between 211 and 235 nm; details can be found in Ref. [13].

$H_2O_2$ /Ar test mixtures were prepared following the procedure previously described [8,9]; key steps are outlined here. A polycarbonate flask that contained approximately 10 g of urea- $H_2O_2$   $[(NH_2)_2CO \cdot H_2O_2]$  powder was placed in a 48 °C water bath. Urea- $H_2O_2$  gradually decomposed to yield  $H_2O_2$  vapor, which was carried into the shock tube test section by a stream of research grade Ar (99.999%). To the knowledge of the authors, urea- $H_2O_2$  was first used as a reliable  $H_2O_2$  source by Ludwig et al. [15]. A typical  $H_2O_2$  concentration of about 2000 ppm can be achieved by setting argon flow rate to be 0.3–0.4 SLPM (standard liters per minute). A stable supply of  $H_2O_2$  at this rate can be generated for approximately 3–4 h.

### 3. Analysis

It has been demonstrated in previous work [8,9] that initial  $H_2O_2$  concentrations can be determined by taking the difference between the final and initial  $H_2O$  levels in a  $H_2O$  profile, as the overall conversion between  $H_2O$  and  $H_2O_2$  is mole-for-mole. In addition, the curvature of  $H_2O$  time-histories is predominately controlled by the rate constant  $k_1$  of reaction  $H_2O_2 + M \rightarrow 2OH + M$  [9].

The combination of OH and  $H_2O$  time-histories provides sufficient information to determine the rate constant for  $OH + H_2O_2 \rightarrow H_2O + HO_2$  ( $k_2$ ) by accessing peak OH concentrations [8]. The rationale is that the OH concentration peaks soon after  $H_2O_2$  decomposition is initiated, at which time species concentrations have the following order:  $[HO_2] \ll [OH] \ll [H_2O_2]$ . Therefore, the OH balance is determined predominately by Reactions (1) and (2).

In contrast,  $H_2O$  time-histories are not sensitive to, and reveal little information regarding,  $k_3$  and  $k_4$  [9]; and although the OH profiles are affected by Reactions (3) and (4), they do not, by themselves, place any strong modeling constraints on these rate constants individually. Additional information regarding the  $H_2O_2$  reacting system becomes essential for accurate evaluation of  $k_3$  and  $k_4$ . Theoretically, the determination of

either  $HO_2$  or  $H_2O_2$  concentration automatically yields the value of the other species by the conservation of hydrogen atoms. In this study we have chosen to use an  $HO_2$  diagnostic because of its stronger sensitivity to  $k_3$  and  $k_4$ .

However, as briefly discussed in the introduction, due to the lack of high-fidelity ultraviolet  $HO_2$  absorption cross-section data at relevant temperatures ( $T > 1000$  K), laser absorption measurements at 227 nm only allow determination of relative shape of  $HO_2$  time-histories. These  $HO_2$  profile shapes provide information about the value of the ratios between  $k_3$  and  $k_4$ , as will become evident in the following section. This information can be further used to infer absolute values of  $k_3$  and  $k_4$  by the addition of information from the OH time-histories, as Reactions (3) and (4) collectively affect OH concentrations. Once absolute values of  $k_3$  and  $k_4$  are determined,  $HO_2$  absorption cross-sections at 227 nm can be calculated.

An iterative fitting approach was used in the analysis rather than a global fitting approach as a global approach would require somewhat arbitrary time-dependent weightings for each species time-history if the same level of sensitivity to each reaction rate constant is to be achieved. Because of this, we do not believe that a global fitting scheme would provide significantly improved final rate constants relative to the iterative approach.

### 4. Results and discussion

Shown in Fig. 1 are example  $H_2O$  and OH time-histories, which provide sufficient information to determine  $k_1$  and  $k_2$  values. Initial conditions in the post-reflected shock wave region were  $T = 1182$  K,  $P = 1.672$  atm. The composition of the initial test mixture was evaluated to

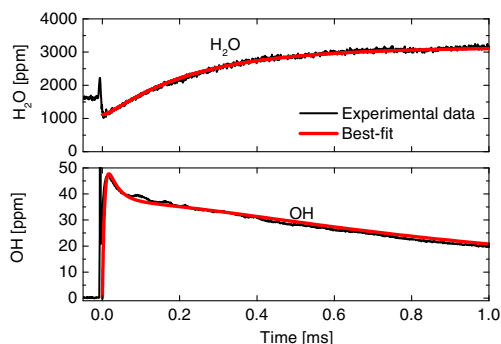


Fig. 1. From  $H_2O$  and OH time-histories,  $k_1$  and  $k_2$  were determined to be  $1.44 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $5.88 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively. The composition of the mixture is 2046 ppm  $H_2O_2$ /1113 ppm  $H_2O$ /556 ppm  $O_2$ /balance Ar.  $T = 1182$  K,  $P = 1.672$  atm.

be 2046 ppm  $\text{H}_2\text{O}_2$ /1113 ppm  $\text{H}_2\text{O}$ /556 ppm  $\text{O}_2$ /balance Ar using the  $\text{H}_2\text{O}$  diagnostic, where  $\text{H}_2\text{O}$  and  $\text{O}_2$  were apparently formed from  $\text{H}_2\text{O}_2$  wall decomposition prior to the arrival of the reflected shock wave, as detailed in our earlier studies [8,9]. It has been shown [9] that the presence of a trace amount of  $\text{O}_2$  only has negligible effects on the kinetics of the  $\text{H}_2\text{O}_2$  thermal decomposition system. The product of the initial  $\text{O}_2$  concentration was estimated from the initial  $\text{H}_2\text{O}$  level by assuming stoichiometric  $\text{H}_2\text{O}_2$  decomposition. For this example case,  $k_1$  and  $k_2$  were determined to be  $1.44 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $5.88 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively, where  $k_1$  is defined as the second-order rate constant. Detailed procedures for inferring  $k_1$  and  $k_2$  have been reported in previous studies [8,9] and are omitted here. Estimated uncertainties in these  $k_1$  and  $k_2$  determinations are  $\pm 23\%$  and  $\pm 17\%$ , respectively.

To determine  $k_3$  and  $k_4$ , the third diagnostic for  $\text{HO}_2$  was introduced. An example laser absorbance time-history measured at 227 nm (radiation from the frequency-quadrupled Ti:Sapphire laser) over a pathlength of 15.2 cm behind a reflected shock wave is presented in Fig. 2, where the absorbance  $\alpha$  was defined by the Beer–Lambert law as  $\alpha = -\ln(I/I_0)$ . The sample laser absorbance profile presents features that are common to all experimental data. Prior to the incident shock wave, a small level of laser absorbance was present due to  $\text{H}_2\text{O}_2$  in the initial mixture, because  $\text{H}_2\text{O}_2$  has a broad absorption spectrum overlapping with the entire  $\text{HO}_2$  spectrum [2]. The mixture was heated to approximately 700 K by the incident shock wave, a temperature too low for any noticeable amount of  $\text{H}_2\text{O}_2$  to decompose during the short period of time ( $\sim 60 \mu\text{s}$ ) before the arrival of the reflected shock wave.

The test mixture was then compressed by the reflected shock wave at time zero; a second jump

in laser absorbance can be again attributed to increased  $\text{H}_2\text{O}_2$  number density. Once the mixture was heated by the reflected shock wave, the rapid  $\text{H}_2\text{O}_2$  decomposition reaction initiated. Two major factors contribute to the evolution of laser absorbance behind the reflected shock wave: the consumption of  $\text{H}_2\text{O}_2$  and the growth and decline of  $\text{HO}_2$ . Laser absorption due to molecular oxygen is negligible (fractional absorption less than  $10^{-4}$  at 227 nm at Fig. 1 conditions), despite the fact that the  $\text{O}_2$  absorption cross-section is strongly temperature-dependent [13]. Total laser absorbance gradually approaches zero as the reaction progresses, confirming that there are no significant absorbing species other than  $\text{H}_2\text{O}_2$  and  $\text{HO}_2$ .

Because  $\text{H}_2\text{O}_2$  consumption is predominantly controlled by Reactions (1) and (2) [8,9],  $\text{H}_2\text{O}_2$  concentration can be determined accurately using information obtained from OH and  $\text{H}_2\text{O}$  time-histories (see Fig. 1). Taking the laser absorbance level right after the reflected shock wave as a reference point, the laser absorbance time-history due to  $\text{H}_2\text{O}_2$  can be calculated (blue curve in Fig. 2). The difference between the total laser absorbance profile and that due to  $\text{H}_2\text{O}_2$  is the  $\text{HO}_2$  absorbance time-history (red curve in Fig. 2). Note that the error in  $\text{HO}_2$  absorbance inherited from the uncertainty in  $\text{H}_2\text{O}_2$  concentration is negligible, because the  $\text{H}_2\text{O}_2$  absorption cross-section is much smaller than that of  $\text{HO}_2$  (approximately an order of magnitude smaller), as will be discussed later.

From  $\text{HO}_2$  absorbance time-histories only relative shapes of  $\text{HO}_2$  profiles can be reliably determined, because the absorption cross-section of  $\text{HO}_2$  is subject to uncertainty. One key parameter to quantify the shape of  $\text{HO}_2$  profiles is the time when  $\text{HO}_2$  concentration decays back to half of its peak value, i.e., the second half-maximum (SHM) point, as denoted in Fig. 2. Similar to FHM points (first half-maximum) or peak points, SHM characterizes the net rates of  $\text{HO}_2$  accumulation and consumption. Additionally, SHM provides much better time resolutions, because FHM and peak points are typically of much shorter time-scales than those of SHM points, due to the “skewed bell shapes” of  $\text{HO}_2$  profiles (see Fig. 2).

In the example case presented in Fig. 2, SHM is observed at 0.34 ms. The dominant source of uncertainty in SHM is the uncertainty in  $\text{H}_2\text{O}_2$  absorbance at time zero, as laser absorbance at time zero is shadowed by shock-induced Schlieren spikes at time zero. Uncertainty in SHM is estimated to be  $\pm 0.03 \text{ ms}$ . With  $k_1$  and  $k_2$  pre-determined from  $\text{H}_2\text{O}$  and OH time-histories, SHM values can be calculated for a wide range of  $k_3$ – $k_4$  combinations at the conditions of Figs. 1 and 2, as presented in Fig. 3. The center line of the shadowed area corresponds to  $\text{SHM} = 0.34 \text{ ms}$ ;

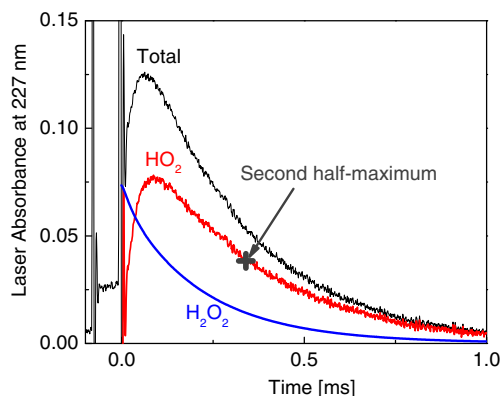


Fig. 2. Example time-history of laser absorbance at 227 nm over a pathlength of 15.2 cm. Conditions are those of Fig. 1.

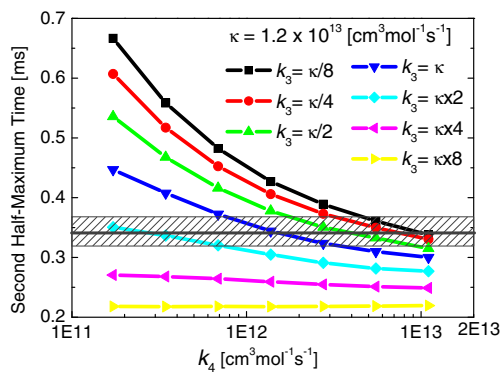


Fig. 3. Predicted second half-maximum (SHM) points of HO<sub>2</sub> profile at the conditions of Figs. 1 and 2. The shadowed area corresponds to SHM = 0.34 ± 0.03 ms as determined from Fig. 2.

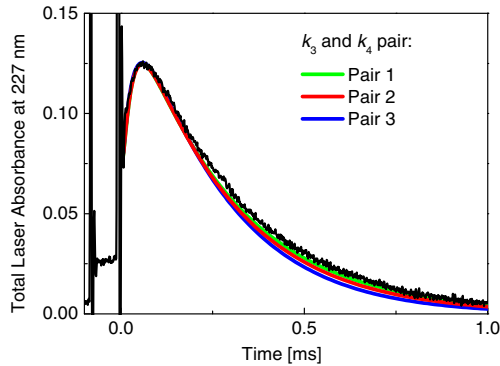


Fig. 4. The experimental laser absorbance at 227 nm can be well-fit by the predictions made with  $k_3$  and  $k_4$  pairs that give SHM = 0.34 ms.  $k_3$ – $k_4$  pairs are listed in Table 1. Test conditions are identical to those of Fig. 1.

whereas the boundaries of the band denote uncertainty limits.

As demonstrated in Fig. 4, the experimental laser absorbance at 227 nm can be well fitted by the predictions made with  $k_3$ – $k_4$  pairs (Table 1) that give SHM = 0.34 ms, where the HO<sub>2</sub> absorption cross-section was chosen for each  $k_3$ – $k_4$  pair by scaling the calculated HO<sub>2</sub> concentrations to match the peak absorbance. Species time-histories were calculated using a recent H<sub>2</sub>/O<sub>2</sub> mechanism

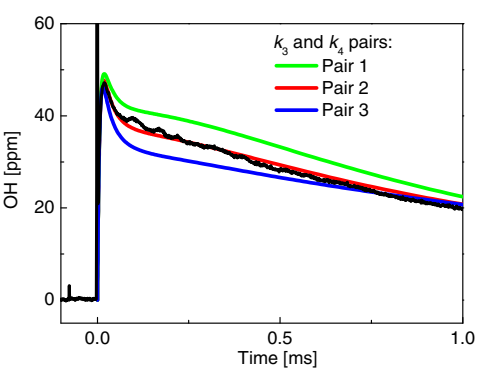


Fig. 5. The unique solution (pair 2) is selected from candidate  $k_3$ – $k_4$  pairs by analyzing the OH time-history. Test conditions are those of Fig. 1.

[14] as the base mechanism, with  $k_1$ – $k_4$  parameters updated to the ones dictated by current experimental data. It may be noted that the small laser absorbance prior to the incident shock wave was due to H<sub>2</sub>O<sub>2</sub> vapor in the initial test mixture.

Although various  $k_3$ – $k_4$  combinations may give very similar shape in HO<sub>2</sub> profile, trends in  $k_3$  and  $k_4$  are opposite for a given SHM (see Fig. 3 and Table 1), which can be utilized to find a unique solution for  $k_3$ – $k_4$ . In Table 1, notice that a 50% change in  $k_3$  leads to less than a 10% difference in predicted peak HO<sub>2</sub> concentrations, as  $k_4$  changes in the reverse direction and compensates for changes in HO<sub>2</sub> concentrations. With an approximately constant HO<sub>2</sub> level, higher  $k_3$  values lead to smaller OH concentrations, because Reaction (3) (OH + HO<sub>2</sub> → H<sub>2</sub>O + O<sub>2</sub>) directly removes OH radicals from the reacting system. The second pair of the  $k_3$ – $k_4$  combinations listed in Table 1 yields the best agreement with the experimental OH time-history, as demonstrated in Fig. 5. Therefore,  $k_3$  and  $k_4$  can be uniquely determined to be  $1.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $1.2 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively. Note that  $k_2$ , the rate constant of Reaction (2) (OH + H<sub>2</sub>O<sub>2</sub> → H<sub>2</sub>O + HO<sub>2</sub>), was mainly inferred from OH concentrations at the peak [8]. Also note that a constant pressure reactor is assumed behind the reflected shock wave, as discussed in Ref. [8].

Uncertainty in  $k_3$  and  $k_4$  comes mainly from the fitting process. The uncertainty from determining SHM (shadowed area in Fig. 3) corresponds to

Table 1  
 $k_3$ – $k_4$  pairs that yield SHM = 0.34 ms and the corresponding HO<sub>2</sub> absorption cross-sections that best-fit experimental data as shown in Fig. 2.

	$k_3 [\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}]$	$k_4 [\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}]$	$\sigma_{\text{HO}_2} [\text{cm}^2 \text{ mol}^{-1}]$	Peak HO <sub>2</sub> [ppm]	Best-fit $\sigma_{\text{HO}_2} [\text{cm}^2 \text{ mol}^{-1}]$
Pair 1	$1.0 \times 10^{13}$	$1.6 \times 10^{12}$	$1.4 \times 10^5$	242	$1.17 \times 10^6$
Pair 2	$1.5 \times 10^{13}$	$1.2 \times 10^{12}$		231	$1.27 \times 10^6$
Pair 3	$2.2 \times 10^{13}$	$0.8 \times 10^{12}$		210	$1.41 \times 10^6$



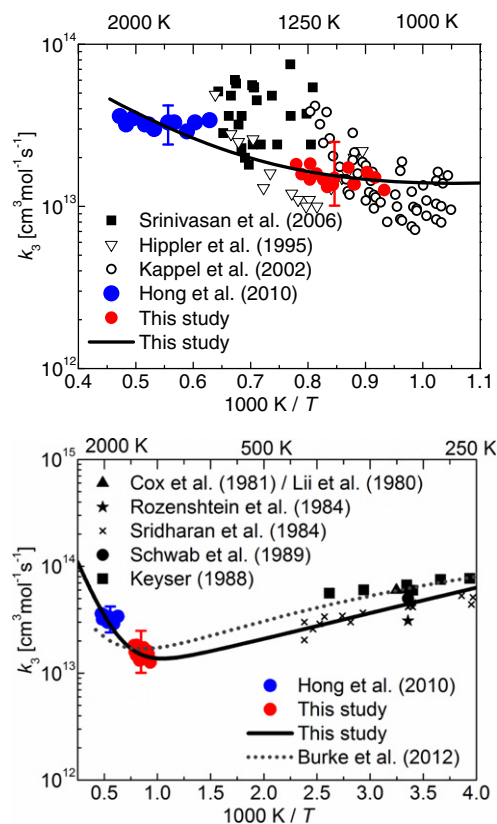


Fig. 6. Arrhenius plot of the rate constants of Reaction (3) ( $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ ).

approximately a factor of 1.6 error in  $k_3$  near  $k_4 = 1.2 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . In addition, the uncertainty in selecting the unique  $k_3$ – $k_4$  pair from fitting the OH time-history is estimated to be a factor of 1.3. Other uncertainty sources, such as temperature uncertainty, are minimized by using  $k_1$  and  $k_2$  parameters determined from experimental data of the same test. As discussed in previous work, the fitting uncertainty in  $k_1$  and  $k_2$  is on the order of 10% and can be neglected here. The overall fitting uncertainty in  $k_3$  and  $k_4$  is therefore estimated to be a factor of 1.67.

Tests were performed behind reflected shock waves at temperatures between 1072 and 1283 K, where the upper temperature limit was set by the need to determine the initial post-shock absorbance by  $\text{H}_2\text{O}_2$  prior to reaction. As demonstrated in Fig. 2, the initial rise in laser absorbance at 227 nm becomes too rapid to be separated from the shock-induced Schlieren spikes at time zero if temperature is too high. Results for  $k_3$  and  $k_4$  are summarized in Arrhenius form in Fig. 6 and 7, respectively. Strong temperature dependency of the rate constant of Reaction (3) ( $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ ) at temperatures near 1100 K has been reported in previous studies [4,5]. However, our

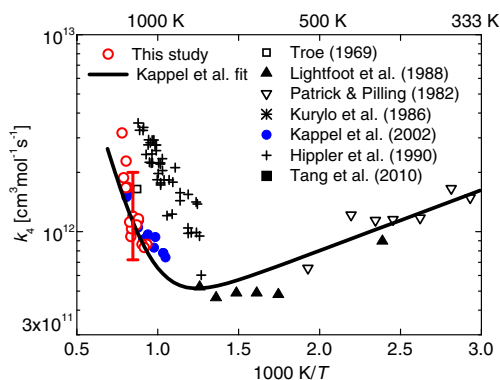


Fig. 7. Arrhenius plot of the rate constants of Reaction (4) ( $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ ).

recent study suggests that  $k_3$  does not have a strong temperature dependency at temperatures above 1600 K [6]. The lack of strong temperature dependency is supported by the current work, as evidenced by the upper panel of figure is 6. It worth noting that there is in fact relatively good agreement between the current work and Hippler et al. [4] and Kappel et al. [5] though there is larger scatter in the two earlier investigations. In addition, a recent theoretical study by Burke et al. [16,17] reported  $k_3$  values that pass through the current work (Fig. 6).

A summation of two Arrhenius expressions can accurately represent the results of the current study, our previous one [6], as well as the studies at low temperatures [18–23]:

$$k_3 = 7.0 \times 10^{12} \exp(550/T) + 4.5 \times 10^{14} \times \exp(-5500/T)$$

and is shown as a solid black line in Fig. 6.

The rate constant of Reaction (4) ( $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ ) has been the subject of many studies near room temperatures, for example, a study by Kurylo et al. [24] and a recent one by Tang et al. [25] between 253 and 323 K (and references therein). However, only a few studies have been reported at elevated temperatures: the study by Patrick and Pilling between 298 and 510 K [26], by Lightfoot et al. between 298 and 777 K [27], and studies near 1100 K [1,3,5]. Results of the current investigation are in good agreement with those reported in the literature [1,5], and therefore the expression recommended by Kappel et al. is kept unchanged:

$$k_4 = 1.0 \times 10^{14} \exp(-5556/T) + 1.9 \times 10^{11} \times \exp(709/T) [\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}].$$

The absorption coefficients of  $\text{H}_2\text{O}_2$  were determined behind both the incident and reflected

shock waves for each test following the procedure outlined earlier in this section. In the post-incident-shock region, the measured absorption cross-section of  $\text{H}_2\text{O}_2$  at 227 nm can be represented by its mean value  $\sigma_{\text{H}_2\text{O}_2}$  (683 K) =  $(1.1 \pm 0.1) \times 10^5$  [cm<sup>2</sup>/mol]. Similarly, the mean  $\text{H}_2\text{O}_2$  absorption cross-section behind reflected shock waves is evaluated to be  $\sigma_{\text{H}_2\text{O}_2}$  (1195 K) =  $(1.4 \pm 0.1) \times 10^5$  [cm<sup>2</sup>/mol] at the same wavelength. The mean absorption cross-section of  $\text{HO}_2$  at 227 nm is estimated to be  $\sigma_{\text{HO}_2}$  (1195 K) =  $(13.1 \pm 1.2) \times 10^5$  [cm<sup>2</sup>/mol]. A dedicated study of  $\text{H}_2\text{O}_2$  and  $\text{HO}_2$  absorption cross-sections over a wide range of wavelengths in the vacuum-UV region is currently underway and will be reported in a future paper.

## 5. Conclusions

Given the importance of these hydrogen peroxide and hydroperoxy reactions in combustion kinetics, it is desirable to more fully characterize the  $\text{H}_2\text{O}_2$  thermal decomposition system. Three laser absorption diagnostics,  $\text{H}_2\text{O}$  detection near 2.5  $\mu\text{m}$ , OH at 306.7 nm, and  $\text{HO}_2$  at 227 nm, were used simultaneously to study  $\text{H}_2\text{O}_2$  thermal decomposition behind reflected shock waves. With  $\text{H}_2\text{O}$  and OH diagnostics, the rate constants for reactions  $\text{H}_2\text{O}_2 + \text{M} \rightarrow 2\text{OH} + \text{M}$  ( $k_1$ ) and  $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$  ( $k_2$ ) can be, and have been, reliably determined. With the addition of an  $\text{HO}_2$  diagnostic at 227 nm, the important species involved in the  $\text{H}_2\text{O}_2$  thermal decomposition reacting system have been measured for the first time in the temperature range covered by the current work. Specifically, the rate constants of reactions  $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$  ( $k_3$ ) and  $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$  ( $k_4$ ) can be inferred from the second half-maximum points (SHM) on  $\text{HO}_2$  laser absorbance time-histories and OH concentrations.

A number of tests were performed at temperature between 1072 and 1283 K and at pressures near 1.7 atm. In contrast to the stronger temperature dependence reported in previous studies [4,5], a weaker temperature dependence for the rate constant of  $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$  was found in this work. The rate constants of reaction  $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$  determined in this work agree very well with those reported by Kappel et al. [5]; the recommendation therefore remains unchanged.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.proci.2012.06.108>.

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