

# A new shock tube study of the $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ reaction rate using tunable diode laser absorption of $\text{H}_2\text{O}$ near $2.5 \mu\text{m}$

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Available online 19 September 2010

## Abstract

The rate coefficient of the reaction  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$  was determined using tunable diode laser absorption of  $\text{H}_2\text{O}$  near  $2.5 \mu\text{m}$  behind reflected shock waves over the temperature range 1100–1530 K, at approximately 2 atm. Detailed kinetic analysis of the recorded  $\text{H}_2\text{O}$  temporal profiles yielded the rate coefficient expression:  $k = (1.12 \pm 0.08) \times 10^{14} \exp[(-7805 \pm 90)/T] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , with estimated uncertainties of  $\pm 4.6\%$  at 1500 K and  $\pm 8.8\%$  at 1100 K. Excellent agreement between this study and that of Masten et al. (1990) was found in the overlapping temperature range. By combining the results of these two studies, the reaction rate coefficient over the range 1100–3370 K was found to be described well by:

$$k = (1.04 \pm 0.03) \times 10^{14} \exp[(-7705 \pm 40)/T] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

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*Keywords:* Laser absorption; Shock tube; Hydrogen; Tunable diode laser

## 1. Introduction

The chain branching reaction between atomic hydrogen and molecular oxygen  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$  (Rxn. 1) is one of the most important elementary reactions in combustion and has been the subject of many experimental studies and reviews [1–14].

In 1973, Schott [3] inferred the rate coefficient of this reaction ( $k_1$ ) from chemiluminescence measurements of O–CO recombination in shock

heated  $\text{H}_2/\text{CO}/\text{O}_2/\text{Ar}$  mixtures at temperatures of 1250–2500 K. For many years Schott's approach appeared to be the most direct and his results were heavily weighted in the subsequent review by Warnatz [15]. In the decade following publication of the early reviews [15,16], more quantitative and direct diagnostics methods were adopted to investigate  $k_1$ . Atomic resonance absorption spectroscopy (ARAS) was used to monitor the time-histories of atomic hydrogen [5,7,8] or atomic oxygen concentrations [4,5] and other groups [6,9–14] applied CW ring-dye laser absorption spectroscopy techniques to measure OH radical time-history profiles and derive the rate coefficient of this reaction.

At temperatures above 1500 K,  $k_1$  was mainly determined from OH time-histories in shock-heated  $\text{H}_2/\text{O}_2/\text{Ar}$  mixtures. Despite similarities in

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the experiments, discrepancies among the early studies [5,6,9,13] are as high as a factor of two at 2000 K. Subsequent studies helped to resolve these discrepancies. Yu et al. [13] reanalyzed the OH data from a previous study by Yuan et al. [10] and recovered results that supported the measurements of Masten et al. [9]. Yang et al. [12] suspected that there were air leaks in the shock tube in the previous  $k_1$  study from the same laboratory [6] and reinvestigated the rate with another shock tube. Their new results again coincided with the rate expression given Masten et al. [9]. Du and Hessler [11] extended the measurements of  $k_1$  to temperatures as high as 5300 K and again confirmed the results in Ref. [9]. The more recent study by Ryu et al. [14] and by Hwang et al. [17] obtained almost identical  $k_1$  values of the previous researchers [9–13] over the range 1500–2500 K using laser absorption spectroscopy of OH radical.

At lower temperatures ( $T < 1500$  K), however, disagreement still exists among the reported values [4,7,8,14,17]. At 1100 K,  $k_1$  from Pamidimukala et al. [4] is approximately 65% of the rate coefficients recommended by other researchers [8,14]. The determinations of  $k_1$  at temperatures lower than 1500 K relied heavily on the ARAS method [4,7,8], and these measurements typically resulted in relatively large scatter (16% and 27% as reported in Refs. [7,8], respectively). In contrast, measurements using OH laser absorption [14,17] yield much smaller scatter in the inferred  $k_1$  values (e.g., 6% as reported in Ref. [14]). However, at lower temperatures, it is difficult to accurately determine  $k_1$  from OH profiles due to complications discussed later in the paper. As pointed out by Hwang et al. [17], a factor of 1.3 discrepancy exists between the two methods [7,14] at 1050 K. An alternative approach of examining  $k_1$  with smaller scatter and better accuracy is desired at temperatures below 1500 K.

Tunable diode laser absorption spectroscopy of H<sub>2</sub>O near 2.5  $\mu\text{m}$  has recently been successfully employed to study the thermal decomposition rate of H<sub>2</sub>O<sub>2</sub> behind reflected shock waves [18]. Using the same H<sub>2</sub>O diagnostic method, simulations using the detailed chemical kinetics model GRI-Mech 3.0 [19] and the Senkin [20] kinetics code show that  $k_1$  can be very accurately determined using the maximum slope of H<sub>2</sub>O profiles in very dilute fuel-rich H<sub>2</sub>/O<sub>2</sub>/Ar reflected shock wave experiments.

Here we present measurements of  $k_1$  for temperatures of 1100–1500 K using the new H<sub>2</sub>O diagnostic method developed in this laboratory. We also provide a comparison with previous studies of this reaction and review the influence that improved measurements [21] of the rate coefficient of reaction (2)  $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$  and the enthalpy of formation of OH [22,23] have on  $k_1$ .

## 2. Experimental setup

Experiments were carried out in a high-purity, 304 stainless steel shock tube with inner diameter of 14.13 cm. The driven section of the shock tube is 8.54 m long, and the driver is 3.35 m long. A detailed description of the shock tube can be found in a previous study [18]. The temperatures behind the incident and reflected shocks, which are denoted as  $T_2$  and  $T_5$  respectively, were calculated using the normal shock equations. Uncertainty in  $T_5$  at time zero is  $\pm 0.8\%$  [24], resulting primarily from uncertainty in the measured incident shock velocity.

Compared to the uncertainty in initial  $T_5$ , temperature variations at longer test times can result in a larger uncertainty in  $k_1$ . Non-ideal flow effects in shock tubes, such as boundary layer growth, finite diaphragm-opening time, etc. can be responsible for the pressure and temperature variations seen at longer times [25]. For the shock tube used in this study, a typical pressure rise rate of 2%/ms is seen near the end section. The test time needed for H<sub>2</sub> oxidation at the fuel concentrations of the current study near 1100 K is 5 ms, therefore the departure from the usual constant U–V model could be as high as 25 K by the time the plateau level of H<sub>2</sub>O is reached.

To reduce (or eliminate) effects of the facility-related increase in pressure and temperature behind reflected shock waves, the shock tube was modified by inserting a cone-shaped obstacle into the driver section [25]. Expansion waves reflected from the surface of the driver insert continuously propagate downstream into the driven section. The gentle decrease in pressure caused by these expansion waves is superimposed on the slow pressure rise related to the boundary layer growth, effectively eliminating the change in pressure and temperature. Uniform pressure profiles obtained in experiments are shown in Section 3.

Test gas mixtures were prepared manometrically (MKS Baratron capacitance manometer) in a stainless steel mixing tank equipped with a magnetic stirrer and turbomolecular pump. Research-grade gases (99.999%) supplied by Praxair were used. The Baratron has a precision better than 0.01 Torr for pressures under 100 and 0.1 Torr for greater pressures. Following the double dilution procedure, two test gas mixtures were prepared: 0.1% O<sub>2</sub>, 0.9% H<sub>2</sub>, balance Ar for tests at higher temperature (1250–1500 K), and 0.1% O<sub>2</sub>, 2.9% H<sub>2</sub>, balance Ar for tests at lower temperatures (1100–1250 K). The relative uncertainty in the test mixture compositions is less than 1%.

The water concentration histories were measured using tunable diode laser absorption of water at 2550.96 nm (3920.09  $\text{cm}^{-1}$ ) within the  $\nu_3$  fundamental vibrational band. This transition was selected because of its large line strength

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